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Formation and Sintering of Pt Nanoparticles on Vicinal Rutile TiO_2 Surfaces

Felix Rieboldt [a], *Stig Helveg* [b], *Ralf Bechstein* [a],*Lutz Lammich* [a], *Flemming Besenbacher* [a],

Jeppe Vang Lauritsen [a], *and Stefan Wendt* [a] *

[a] Interdisciplinary Nanoscience Center (iNANO), Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark

[b] Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark

***Corresponding Author**

E-mail: swendt@phys.au.dk

Abstract

By means of scanning tunnelling microscopy (STM) the nucleation, growth and sintering of platinum nanoparticles (Pt NP's) was studied on vicinal and flat rutile titanium dioxide (TiO_2) surfaces. Utilising physical vapour deposition, the nucleation of Pt NP's on TiO_2 surfaces at room temperature (RT) was found to be random and invariant towards different surface morphologies and reduction states. Thus, the nucleation of Pt on TiO_2 at RT is rather insensitive to the surface structure and surface defects. Vacuum-annealing at 600 K, 700 K and 800 K, respectively, led to lower densities of Pt NP's as a result of sintering. Sintering occurred at different rates at the TiO_2 surfaces studied, indicating that the surface morphology and the amount of Ti^{3+} excess charge do have an influence on the particle stability. Observed changes in the NP distribution as a result of sintering can be explained inferring facile diffusion of Pt NP's along the [001] direction.

1 Introduction

Owing to their technological applications in heterogeneous catalysis and photocatalysis, supported transition metal nanoparticles (NP's) have been studied intensely.[1-6] Specifically, much research has been focused on Platinum (Pt) NP's dispersed on metal oxide supports which are used in automotive converters to reduce the emission of environmentally harmful gases such as carbon monoxide (CO) and nitrogen oxides (NO, NO_2).[7-12] In automotive converters, high temperatures and pressures are commonly used, which leads to sintering of the NP's. Accordingly, NP's are agglomerated into larger NP's, which leads to a decline in catalytic reactivity due to loss of active surface area.[13, 14] Sintering is a complex process that occurs following various mechanisms, or combinations of them. The prevailing mechanism depends on the exact materials combination of the metal NP's and the support (usually oxides), the gases involved in the reaction(s), the temperature, the structure of the NP's and the interaction between the NP's and the oxide support.[3, 14-16] A number of studies have previously been conducted addressing the mechanism of sintering, e.g. considering Pt NP's on silica and alumina supports.[17-19] In these studies, Ostwald ripening has been found to be the prevailing mechanism for the sintering of Pt NP's. However, the oxide support plays an important role, and for different oxide supports the sintering kinetics and the prevailing sintering mechanism may be different as well. Studies regarding the influence of the oxide support have been proven to be difficult because of lacking control of the surface structure. The present study compares the nucleation, growth and sintering of Pt NP's on various rutile titania (TiO_2) surfaces with different surface morphology and surface reduction states.

TiO_2 is a typical oxide support material in various applications, ranging from gas sensors, photovoltaics, heterogeneous catalysis and photocatalysis to the photogeneration of hydrophilic oxide films.[20-22] In addition, TiO_2 has become the most studied transition metal oxide in surface science [21-25] because rutile TiO_2 crystals of high quality can be synthesized. Specifically, the rutile TiO_2 (110)–(1 × 1) surface has been studied intensely, and many interesting surface phenomena have been unravelled by using traditional surface science techniques and STM measurements.[21-25] In previous STM studies by Wendt and co-workers, both the adsorption of molecules such as water, oxygen and ethanol [23, 26-30] and the nucleation of Au and Ag NP's[31-33] have been studied.

Several previous experimental and theoretical surface science studies addressed the nucleation, growth and sintering of Pt NP's on TiO_2 surfaces and revealed interesting insights.[34-49] For example, Gan *et al.* concluded that the surface structure of TiO_2 (110) plays a crucial role and that the (1 × 2) reconstructed surface exhibits a stronger interaction with Pt than the (1 × 1) surface.[34] Nevertheless, a conclusive understanding of the Pt-TiO_2 support interaction has not yet been achieved, and contradictory results have been reported regarding the preferred nucleation site of Pt atoms on the rutile TiO_2 (110) surface. Previous STM studies revealed random positioning of Pt NP's on the rutile TiO_2 (110) surface.[34-36] Inspired by Isomura *et al.*'s STM study,[36] Jiang *et al.* considered in their density functional theory (DFT) calculations Pt NP's consisting of 4 to 8 Pt atoms.[37] All these small Pt NP's were found to be centred about the Ti troughs on the TiO_2 (110)–(1 × 1) surface. In another theoretical study by Çakir *et al.* it has been reported that bridging oxygen vacancies (O_{br} vac.'s) serve as nucleation sites for Pt NP's on rutile TiO_2 (110);[38] however, direct experimental evidence for this prediction has not been provided.

Another interesting issue that needs to be considered for Pt-TiO_2 systems is the strong metal - support interaction (SMSI).[50] The SMSI effect occurs upon reduction of Pt-TiO_2 and leads mostly to decreased catalytic activity.[40-42, 51-55] The SMSI effect has been explained by encapsulation of Pt NP's on the TiO_2 support by a reduced TiO_x over-layer.[40-43, 53, 56] For small Pt particles down to atomic Pt the SMSI effect has been observed in UHV following annealing at 700 K.[45, 47] However, while Gan *et al.* reported evidence for encapsulation of Pt NP's on TiO_2 (110)–(1 × 1), they did not find evidence for encapsulation of small Pt NP's supported on a (1 × 2) reconstructed TiO_2 (110) surface, even after annealing at 770 K.[34]

In the present study, STM results on the nucleation and sintering of Pt NP's on various rutile TiO_2 surfaces are presented. Four different TiO_2 surfaces are compared that differ (i) in their density of prevailing step edges and (ii) in their surface reduction states. The TiO_2 surfaces were imaged directly following Pt evaporation at RT and, additionally, following vacuum-annealing at elevated temperatures to induce sintering. Conclusions are drawn on the nucleation and sintering behaviour of Pt NP's depending on the surface morphology and surface reduction of the support. It is found that neither the surface morphology nor the surface reduction state of the TiO_2 samples strongly influence the nucleation of Pt at RT. Annealing the samples led to NP sintering resulting in larger Pt NP's, and differences were found regarding the Pt NP distributions on the TiO_2 supports compared. Based on these differences it is inferred that anisotropic surface diffusion of Pt NP's or atomic Pt species in the [001] direction is dominant.

2 Experiments

All the experiments were carried out in a UHV system (SPECS, Germany) consisting of two separable chambers, one for STM analysis and one for sample preparation and Pt evaporation. The base pressure was below 1×10^{-10} mbar in both chambers. The UHV system was equipped with an Aarhus-150 STM (SPECS), an X-ray source (SPECS), a helium discharge lamp (Thermo Fischer, UK), a hemispherical energy analyser (SPECS, PHOIBOS) and an electron beam evaporator for Pt evaporation (SPECS).

Two flat rutile TiO_2 (110) samples were used as well as two TiO_2 (110) samples that were intentionally miss-cut by ~3° either perpendicular to or along the [001] direction (see Fig. 1). All four samples originated from the same batch (SurfaceNet). The slightly miss-cut TiO_2 (110) single crystals provided two vicinal TiO_2 (110) surfaces: (i) TiO_2 (870) with a high density of [001] step edges and (ii) TiO_2 (771) with a high density of $\left[1\bar{1}1\right]$ and $\left[1\bar{1}\bar{1}\right]$ step edges.[57, 58] The two vicinal surfaces and one of the flat TiO_2 (110) surfaces were similarly prepared by continuous cycles of Ar^+ sputtering (10 min, 5×10^{-7} mbar, 1.5 keV, 10 mA) and 15 min vacuum-annealing at (910 ± 10) K. At the beginning of the experiments, the flat TiO_2 (110) surface was prepared by ~90 cycles of sputtering and annealing, while the two vicinal surfaces [(870) and (771)] were prepared by ~60 preparation cycles. Based on UPS measurements these three samples were assessed to be highly reduced.[58] In order to distinguish between the flat TiO_2 (110) surface that was prepared already ~90 times and a second flat TiO_2 (110) surface that was much less reduced, the highly reduced surface will be denoted as HR-TiO_2. The second flat TiO_2 (110) sample was prepared only ~20 times at the beginning of the experiments and this sample was vacuum-annealed at only (855 ± 10) K. As shown previously,[26, 59, 60] this preparation leads to a slightly reduced surface, and accordingly, this surface is referred to as SR-TiO_2. During sample preparation, ramps of 1 K/s were used upon heating and cooling of the samples. The sample temperature was measured using a K-type thermocouple and double checked using a pyrometer.

Pt was deposited via e-beam evaporation with the TiO_2 samples at 300 K. Subsequently, the samples were annealed for 5 min either at 600 K, 700 K or 800 K. Between the different experiments the TiO_2 surfaces were cleaned by four cycles of sample preparation to remove the Pt from the previous experiment. By means of XPS it was verified that the surfaces were indeed free of Pt and that identical amounts of Pt were evaporated onto the surfaces. The Pt coverage was determined by XPS using the ratio of the integrated Pt 4f and Ti 2p peak areas.[34, 61] A monolayer matrix factor $Q^{Pt}_{\mathbf{Ti}}$ of ~3.7 was taken into account with a mean free electron path λ of ~1 nm and a layer thickness d_{Pt} in Pt of ~0.27

nm.[61, 62] Additionally, XPS measurements before and after the annealing treatments showed that the amount of Pt on the surfaces did not change through the annealing at higher temperatures, i.e. that no Pt was lost (Fig. S1). The UPS measurements were conducted using He I irradiation (21.21 eV) at 100–120 K. The valence band (VB) spectra were normalized such that the intensities at ~10 eV binding energy (BE) were equal in all spectra. This allowed a direct comparison of the VB spectra and the integrated areas of the gap state (GS). STM measurements were conducted in the constant current mode (bias voltage ~1.2 V, tunnelling current ~0.1 nA) with the sample kept similarly at a low temperature of 90–110 K.

3 Results

Figure 2 presents STM images and valence band spectra of the flat HR-TiO_2 (110) surface and the two vicinal surfaces, TiO_2 (870) and TiO_2 (771), respectively. STM images (60 nm × 60 nm) of the three clean surfaces are shown in Fig. 2(a)-(c), whereas typical valence band (VB) spectra are presented in Fig. 2(d)-(f). For all STM images, a periodic colour scale with a periodicity of one atomic layer on the TiO_2 (110) surface, i.e. ~0.33 nm, was used to illustrate the (110) terraces with the same colour gradient. The terraces are characterized by alternating rows along the [001] direction of in-plane, fivefold-coordinated Ti atoms (bright rows) and bridging oxygen atoms (O_{br}, dark rows). Within the O_{br} rows, the O_{br} vac.'s can be seen as faint, bright spots.[22-24] The flat TiO_2 (110) surface was characterized by large terraces (and thus, a high density of O_{br} vac.'s) [55] and rather few step edges [Fig. 2(a)], whereas the two vicinal surfaces showed narrow terraces and high step edge densities. Particularly, the TiO_2 (870) surface was characterized by a high density of [001] steps [Fig. 2(b)], whereas a high density of $\left[1\bar{1}1\right]$ and $\left[1\bar{1}\bar{1}\right]$ steps dominated the TiO_2 (771) surface [Fig. 2(c)].[57, 58]

Whereas the $\left[1\bar{1}1\right]$ step edges are reduced,[63-66] no O vac.'s are stabilised along the [001] steps.[65-67] Additionally, a high amount of elongated strands in the [001] direction (elliptic mark) were present on the (771) surface.[57, 58] These strands are reduced ad-structures connected to the $\left[1\bar{1}1\right]$ steps that grow on the lower terrace with a periodic centre-part and a more protruding end-structure (see Fig. 1). The strands are a possibility to compensate for missing O atoms and thus, they are competitive to point defects such as O_{br} vac.'s and Ti interstitials.[57] The strands are characteristic of the (771) surface and occur at all reduction states.[57, 58] The VB spectra in Fig. 2(d)-(f) were acquired at comparable bulk reduction states, i.e. after applying the same number of preparation cycles. The differences in the VB spectra between the three surfaces arose from the different surface morphologies.[57, 58] The GS (see inserts) originates from Ti^{3+} excess charge and its integrated area is considered a measure for the surface reduction.[26, 60, 68] The flat TiO_2 (110) surface showed a significantly larger GS than the two vicinal surfaces, indicating a higher surface reduction of this surface compared to the other two TiO_2 surfaces.

Figure 3 shows a panel of STM images acquired after depositing ~0.1 ML of Pt at RT onto the three TiO_2 surfaces considered [Fig. 3(a)-(c)], and after annealing of the samples in UHV for 5 min at either 600 K [Fig. 3(d)-(f)], 700 K [Fig. 3(g)-(i)] or 800 K [Fig. 3(k)-(m)], respectively. Following Pt evaporation at RT [Fig. 3 (a)-(c)], a considerable amount of Pt NP's have nucleated on all TiO_2 surfaces considered. The average apparent height of the Pt NP's was consistently 0.33 ± 0.04 nm on these TiO_2 surfaces, in good agreement with the literature.[36, 49] Likewise, the densities of Pt NP's were comparable on the TiO_2 (110), (870) and (771) surfaces with a value of 1.2 / nm^2. Furthermore, the Pt NP's were distributed similarly on all three surfaces, i.e. their distributions were homogeneous across the surfaces and there was no obvious preference for Pt NP's to nucleate at step edges or on terrace sites. On the TiO_2 (771) surface, Pt NP's appeared also on top of the strands [Fig. 3(c)].

Upon annealing the samples, the density of Pt NP's declined on all three surfaces from 1.2 / nm^2 to below 0.5 / nm^2, and the average Pt NP height increased from 0.33 ± 0.04 nm to 0.47 ± 0.07 nm. XPS measurements on the clean TiO_2 surface, after Pt deposition and after annealing revealed that the Pt coverage remained constant and that no Pt was lost upon annealing (Fig. S1). This result is in line with previous studies on Pt NP's on TiO_2 (110).[39] The Pt NP's in Fig. 3(k)-(m) were larger compared to those seen in Fig. 3(a)-(c). In particular, the particles marked by black squares in Fig. 3(k)-(m) were higher than two atomic layers of TiO_2 on TiO_2 (110) (i.e. 0.66 nm, note the periodic colour scale) and on all three surfaces several of these high NP's were found following annealing at 800 K. Note that such high NP's were not observed directly after Pt deposition (average height 0.33 ± 0.04 nm) and that the number of these high NP's was lower on the (870) surface compared to those observed on the (110) and (771) surfaces.

Following vacuum-annealing the samples at 600 K, 700 K and 800 K, respectively, different geometric distributions of the Pt NP's were found on the three surfaces considered. Whereas the Pt NP's remained distributed homogeneously on the (110) and (870) surfaces even after annealing at 800 K [Fig. 3 (k),(l)], the distribution of the Pt NP's changed considerably on the (771) surface. Here, following annealing at 800 K, the Pt NP's were found almost exclusively along $\left[1\bar{1}1\right]$ step edges and on top of the strands [Fig. 3(m)].

Figure 4 compares annealing experiments conducted with the HR-TiO_2 (110) surface (left column) and the SR-TiO_2 (110) surface (right column). The STM images of the HR-TiO_2 surface were selected from the same data set that was used for compiling Fig. 3. The second TiO_2 (110) crystal was prepared by using fewer cycles of sputtering, and annealing and lower annealing temperatures were used than for preparing the HR-TiO_2. This resulted in a lower surface reduction state and a lower O_{br} vac. density on the SR-TiO_2 surface (cf. Fig. 5). Specifically, the HR-TiO_2 surface was characterized by ~10-11 % monolayer (ML) O_{br} vac. density, where 1 ML is defined as the density of (1 × 1) unit cells on the TiO_2(110) surface, i.e. 5.2×10^{14} / cm^2. The SR-TiO_2 was characterized by ~7 % ML O_{br} vac. density. Following Pt evaporation and annealing, the Pt NP distributions found on the SR- and HR-TiO_2 surfaces were comparable. However, the total NP density was lower on SR-TiO_2 than on HR-TiO_2 following annealing at 800 K [Fig. 4(g),(h)].

Figure 6 presents another interesting result obtained for the TiO_2 (771) surface. On the clean TiO_2 (771) surface [Fig. 6(a)], a ~1.5 nm wide gap exists between the strand end-structures and the following step edges.[57, 58] After Pt evaporation and annealing at 800 K [Fig. 6(b)], Pt NP's were found preferentially along the step edges on the upper terraces (circle) and on top of the strands. Interestingly, Pt NP's at the end of the strands (square) "extended" the strands all the way to the step edges. In addition, the Pt NP's on top of the periodical centre-part of the strands (diamonds) were only dilute features and NP's on the terraces were very rare.

Figure 7 illustrates the decrease in NP density on the various TiO_2 surfaces as function of the annealing temperature. For each data point, six STM images of 60 nm × 60 nm large areas were analysed. Directly after Pt evaporation at RT (300 K), the NP densities were within the error bars comparable at ~1.2 / nm^2 for all four TiO_2 surfaces. Annealing at 600 K led to similarly decreased densities of Pt NP's of ~0.65 / nm^2 on the HR-TiO_2 (black circles, continuous line), the SR-TiO_2 (yellow triangles, dashed line) and the TiO_2 (771) surface (green triangles, continuous line), respectively. Only for the TiO_2 (870) surface (blue circles, dashed line) the density of NP's was higher than on the other surfaces (~0.9 / nm^2). Following instead annealing at 700 K and 800 K, the densities of Pt NP's decreased on SR-TiO_2

and TiO_2 (771) even further to ~0.5 / nm^2 and ~0.3 / nm^2, respectively. A similar monotonic decrease in NP density was observed for the TiO_2 (870) surface. However, on this surface the density of Pt NP's was still ~0.5 / nm^2 even after annealing at 800 K. On HR-TiO_2, the measured density of Pt NP's following annealing at 700 K was still the same as found following annealing at 600 K (~0.65 / nm^2). This value coincides with the NP density found on the (870) surface following annealing at 700 K. Following annealing at 800 K, the NP densities on the HR-TiO_2 and TiO_2 (870) surfaces were comparable within error bars. A comparison in total numbers of Pt NP's per 60 nm × 60 nm STM image (right axis) illustrates that the differences were significant between HR-TiO_2 and TiO_2 (870) on the one hand (~180 NP's per STM image), and SR-TiO_2 and TiO_2 (771) on the other hand (~110 NP's per STM image).

In a more detailed analysis it was also considered where exactly the Pt particles appeared upon annealing on the four TiO_2 surfaces considered (Fig. 8). It was distinguished between step edges (yellow bars), terraces (blue bars) and, in the case of the TiO_2 (771) surface, strands (grey bars). In the latter case, it was further distinguished whether the Pt NP's resided at the end of the strands (light grey bars) or on top of the periodic centre-parts (dark grey bars). Figure 8(a) presents the corresponding Pt NP densities for each sample and annealing temperature, whereas Fig. 8(b) shows the relative NP densities, i.e. which percentages of the Pt NP's were found at step edges, terraces and strands, respectively. Figure 8(b) shows that the NP distributions were similar on the two flat TiO_2 (110) surfaces and that most of the Pt NP's appeared on the terraces on these two surfaces at all temperatures (only ~15% of the Pt NP's were found at step edges). In case of the two stepped surfaces, TiO_2 (870) and TiO_2 (771), significant higher percentages of 45-50% of NP's resided at step edges disregarding the annealing temperature. Because of the much higher density of step edges on these vicinal TiO_2 surfaces this result was expected. On the TiO_2 (771) surface, strands cover the narrow terraces and thus, the percentages of Pt NP's on terraces and on strands on the TiO_2 (771) surface need to be compared with the percentage of NP's on terraces on the TiO_2 (870) surface without strands.

Annealing the samples did not lead to remarkable changes of the NP distributions on the two flat TiO_2 (110) surfaces and the TiO_2 (870) surface. The number of Pt NP's decreased with increasing annealing temperature [Fig. 7 and Fig. 8(a)] but the percentages of NP's at step edges and on terraces remained the same on these three surfaces. However, the NP distribution on the TiO_2 (771) surface changed considerably upon annealing. Interestingly, the percentage of Pt NP's at step edges increased slightly up to ~60% after annealing at 600 K and 700 K and then dropped to ~50% following annealing at 800 K. The percentage of Pt NP's on terraces decreased monotonically from ~20% to ~5%, whereas the percentage of Pt NP's on strands increased from ~30% to ~45%. This means that most of the Pt NP's on the TiO_2 (771) surface appeared at step edges or strands following annealing at 800 K. Furthermore, a significant change was found regarding the Pt NP's on the strands on the TiO_2 (771) surface. Directly after evaporation at RT, Pt NP's were found both on the centre-parts and on the end-structures with a ratio of about 3 : 2. Following annealing at elevated temperatures, this ratio decreased monotonically as a function of the temperature to ~1 : 8 following annealing at 800 K, meaning that finally most Pt NP's on strands on the TiO_2 (771) surface appeared at the end-structures of the strands. Note, however, that the total number of Pt NP's at strand end-structures was constant in all the experiments [Fig. 8(a), light grey bars, ~50 Pt particles per (60 nm^2) image or ~0.014 / nm^2], whereas the total number of Pt NP's on the (771) surface decreased remarkably with increasing annealing temperature.

It can be inferred from these results that Pt from the NP's on the terraces on the TiO_2 (771) surface have diffused to $[1\bar{1}1]$ step edges, there forming larger NP's, while Pt from the NP's on the strand centre-parts diffused to NP's at the end-structures. Once the Pt reached the end-structures they remained there and the NP's increased in size. Indeed, the largest Pt NP's on the TiO_2 (771) surface following annealing at 800 K [Fig. 3(m)] were the ones at the end-structures rather than those at the step edges. In the annealing experiments on the other TiO_2 surfaces such obvious diffusion from terraces to step edges was not observed. Thus, the strand end-structures on TiO_2 (771) are preferred sites for Pt NP's.

4 Discussions

4.1. Pt Nucleation at RT

For the following discussion, the characteristic differences of the four TiO_2 surfaces need to be taken into account. As mentioned above, the $\left[1\bar{1}1\right]$ step edges dominate the TiO_2 (771) surface, exposing a high density of O vac.'s. Note that O vac.'s (both on the terraces, i.e. O_{br} vac.'s, and at step edges) are generally known as preferential sites for adsorption of molecules[21-25, 64, 65] and nucleation sites of small metal NP's,[5, 31, 33] respectively. In contrast, the [001] step edges that dominate the TiO_2 (870) surface are not reduced.[65-67] However, even though the TiO_2 (771) surface offers a large number of O vac.'s no clear difference between the different surfaces was seen in the STM images acquired after Pt evaporation [Fig. 3(a)-(c)], and the Pt nucleation on the two stepped surfaces was very similar, as seen from the densities (Fig. 7) and the particle distributions (Fig. 8). Furthermore, the differences in relative Pt NP density between the stepped surfaces and the flat TiO_2 (110) surfaces, i.e. 45-50% of Pt at step edges compared to ~15%, can be best explained by the higher densities of step edges on the two former surfaces. From these observations it is concluded that O vac.'s along the $\left[1\bar{1}1\right]$ step edges on the TiO_2 (771) surface did not act as preferred nucleation sites for Pt at RT.

The two flat TiO_2 (110) surfaces differed in their reduction states, resulting in different quantities of Ti^{3+} excess charge in the near surface region and different O_{br} vac. densities on the terraces. If the O_{br} vac.'s and the Ti^{3+} excess charge had a direct influence on the nucleation of Pt at RT, a clear difference between the STM images in Fig. 4(a) and (b) would be expected, and also the NP distributions (Fig. 8) should be different. Nonetheless, no such differences were observed at our samples, indicating that Ti^{3+} excess charge and O_{br} vac.'s are not of high relevance for the nucleation of Pt at the chosen conditions.

Furthermore, the presence of strands on the TiO_2 (771) surface did not have impact on the Pt nucleation at RT. Following Pt evaporation at RT, Pt NP's covered the TiO_2 (771) surface homogeneously without any preference or disfavour for nucleation at the strands [Fig. 3(c)]. However, strand end-structures were found to be preferred sites for Pt NP's after annealing at 800 K, a result that bears similarity to a previous report by Gan *et al,*[34] where preferential nucleation of Pt NP's on a reconstructed TiO_2 (110)–(1 × 2) surface was observed following Pt deposition at RT.[34]

The STM data presented here do not allow drawing clear-cut conclusions as to whether O_{br} vac.'s serve as nucleation sites for Pt nucleation. As described above, the surface reduction state and the density of O_{br} vac.'s did not influence the nucleation of Pt at RT [cf. HR-TiO_2 and SR-TiO_2 (110) surfaces in Fig. 4(a),(b), Fig. 7 and Fig. 8], which does not support the hypothesis of preferential Pt nucleation at O_{br} vac.'s. However, the possibility exists that very small Pt NP's can be stabilized at O_{br} vac.'s and that different preparations than applied here are needed to prepare them. Hence, whether O_{br} vac.'s can serve as preferred nucleation sites for small Pt NP's[38] remains to be clarified. For the Pt NP's studied here, characterized by apparent STM heights of 0.33 ± 0.04 nm, the role of O_{br} vac.'s as nucleation sites seems to be negligible.

4.2. Pt Sintering upon Vacuum-annealing

Following vacuum-annealing at 800 K, Pt NP's on the TiO_2 (771) surface appeared almost exclusively along $\left[1\bar{1}1\right]$ step edges and at strand end-structures. Within a particle or atom migration sintering model on TiO_2 (110)[39] a possible explanation of this result is a variation of the diffusion probabilities of Pt NP's or atomic species on the TiO_2 (110) terraces depending whether they diffuse along or perpendicular to the [001] direction. Assuming a higher diffusion probability along the [001] direction, i.e. along the Ti and O_{br} rows, the sintering of Pt should be different depending on the surface morphology. In case of the TiO_2 (870) surface, Pt diffusion on the terraces would be facilitated parallel rather than perpendicular to the [001] step edges. As a result, upon annealing Pt can diffuse longer distances on the terraces before hitting a step edge. In contrast, Pt on the TiO_2 (771) surface would diffuse almost perpendicular to the dominating $\left[1\bar{1}1\right]$ step edges and thus, reach step edges more frequently than on the TiO_2 (870) surface. Once Pt reached a $\left[1\bar{1}1\right]$ step edge, it may be more strongly bound than on a regular terrace site, or be sterically hindered from further diffusion. This scenario is in line with the increased percentage of Pt NP's at step edges after annealing at 600 K on the TiO_2 (771) surface [see Fig. 8(b)]. Comparing the Pt NP distributions obtained after annealing at 700 K and 800 K, it can be speculated that Pt that already resided at step edges on the TiO_2 (771) surface diffused along the $\left[1\bar{1}1\right]$ step edges, leading to agglomeration of larger NP's. Following annealing of the Pt/TiO_2 (870) surface at 800 K [Fig. 3(l)], about half of the Pt NP's residing at step edges were found at short $\left[1\bar{1}1\right]$ step edges (data not shown), even though the [001] step edges clearly dominate the TiO_2 (870) surface. This result also supports that the diffusion of Pt is most facile along the [001] direction.

Of particular interest is the prevailing mechanism for Pt sintering in the annealing experiments conducted in vacuum. In a previous study by Behafarid and Roldan Cuenya[39] it has been concluded that diffusion-coalescence rather than Ostwald ripening is the dominant sintering mechanism of Pt NP's on TiO_2 (110). As outlined above, a model based on diffusion-coalescence allows explaining that Pt NP's on the TiO_2 (771) surface appeared almost exclusively along $\left[1\bar{1}1\right]$ step edges following annealing at 800 K. The question remains whether all the NP densities obtained in the annealing experiments (Fig. 7) can be explained within the framework of this model. Following annealing at 600 K, the TiO_2 (870) surface showed a smaller decline in NP density (blue dashed line) than the TiO_2 (771) surface and the two flat TiO_2 (110) surfaces, resulting in a higher NP density. This difference may be explained considering that the proportion of Pt NP's on or close to [001] step edges is larger on this TiO_2 surface compared to the other three surfaces and that the mobility of Pt NP's close to these step edges is diminished.

Comparing the Pt NP densities obtained following vacuum-annealing at 600 K, 700 K and 800 K, the NP densities on the TiO_2 (870), TiO_2 (771) and SR-TiO_2 surfaces decreased in a similar fashion (Fig. 7). In contrast, the NP densities on the HR-TiO_2 surface (black solid line) following annealing at 600 K and 700 K were identical, and a decrease on this surface comparable to those on the other surfaces was observed only after annealing at 800 K. We argue that this difference occurred because of the larger amount of Ti^{3+} excess charge available on this surface compared to the other three TiO_2 surfaces that were characterized by smaller GS's, i.e. smaller amount of Ti^{3+} excess charge. However, even though the amount of Ti^{3+} excess charge influences the kinetics of a specific sintering mechanism for Pt NP's on TiO_2, it appears unlikely that the sintering mechanism itself changes because of the higher amount of Ti^{3+} excess charge on HR-TiO_2.

Rather, it can be assumed that the diffusion of Pt NP's or Pt atoms is hindered on HR-TiO_2 (110) because of the higher density of O_{br} vac.'s. However, if this picture is valid, it is not clear as to why the sintering behaviour following annealing at 600 K was comparable on SR- and HR-TiO_2 surfaces. Rather, differences in the sintering behaviours were found only following annealing at 700 K (Fig. 7). One possible explanation is that the diffusion of larger Pt NP's is stronger influenced by O_{br} vac.'s and Ti^{3+} than of smaller Pt NP's. However, this scenario is against chemical intuition, since it is known from Au / TiO_2 (110) that a single O_{br} vac. can stabilize, at maximum, Au_3.[31] Accordingly, we favour another possible explanation, in which the TiO_2 substrate is considered to behave more dynamic. Specifically, we revert to observations in annealing-experiments on oxidized TiO_2 (110) surfaces, where the substantial re-appearance of O_{br} vac.'s was found only for vacuum-annealing at temperatures higher than 600 K (see Fig. S2). Accordingly, assuming for Pt / TiO_2 (110) that O vacancies can be accumulated beneath of Pt NP's, the decreased sintering of Pt NP's following vacuum-annealing at 700 K and 800 K could be understood. Such an accumulation of O vacancies beneath of Pt NP's may precede the encapsulation of Pt NP's by a TiO_x over-layer, as known from the SMSI effect. Further studies are required to better understand the influence of O_{br} vac.'s and Ti^{3+} on the sintering of Pt NP's.

Finally, the SMSI effect has to be considered when discussing the annealing experiments. If the SMSI effect occurred as expected for all Pt NP's upon annealing at 700 K and 800 K[43, 45, 47] the resulting Pt NP's would increase in height to at least ~0.6 nm (~about two atomic layers on TiO_2 (110), i.e. one layer Pt and one layer TiO_x over-layer). However, a large density of small NP's with a maximum height of one atomic layer (0.33 nm) still existed on all four TiO_2 surfaces, even after annealing at 700 K [Fig. 3(g)-(i) and Fig. 4(e),(f)] and 800 K [Fig. 3(k)-(m) and Fig. 4(g),(h)], respectively. Accordingly, if the SMSI effect occurred it did not occur for all Pt NP's, or the Pt NP's were simultaneously buried. Furthermore, an encapsulation of Pt by a TiO_x over-layer should cause changes to the XPS spectra. Following vacuum-annealing, the Pt 4f peak would decrease while the Ti 2p signal would increase. As can be seen in Fig. S1, this was not the case in our experiments. The Pt 4f peak was found to be the same before and after annealing at 800 K. Thus, at the chosen experimental conditions no clear evidence for encapsulation was observed.

5 Conclusions

The nucleation, growth and sintering of Pt NP's on four different TiO_2 (110) surfaces were studied by STM. Two vicinal TiO_2 (110) surfaces were studied, namely TiO_2 (870) and TiO_2 (771) surfaces. These vicinal surfaces were characterized by high densities of [001] step edges [TiO_2 (870)], and $\left[1\bar{1}1\right]$ / $\left[1\bar{1}\bar{1}\right]$ step edges [TiO_2 (771)], respectively. In addition, two flat TiO_2 (110) surfaces of different reduction states were studied. This approach made it possible to compare the nucleation and sintering of Pt NP's depending on the surface morphology and the surface reduction state.

No differences were observed for the nucleation of Pt on these surfaces following Pt evaporation at RT. On all surfaces, on average ~0.33 nm high Pt NP's were found to be homogeneously distributed, and their densities were comparable irrespective of the surface reduction state and the surface morphology. Thus, the nucleation and growth of Pt on TiO_2 at RT is insensitive to surface defects such as O_{br} vac.'s, strands and the presence of Ti^{3+} excess charge beneath the terraces.

Following vacuum-annealing of the samples at 600 K, 700 K and 800 K, respectively, the Pt NP's increased in size and their number decreased considerably as a result of sintering. Whereas the distributions of NP's on the two flat TiO_2 (110) surfaces and the TiO_2 (870) surface remained homogeneous even after annealing at 800 K, Pt NP's on the TiO_2 (771) surface were almost exclusively found along the $\left[1\bar{1}1\right]$ and $\left[1\bar{1}\bar{1}\right]$ step edges and on strand end-structures following annealing at 800 K. It is inferred that Pt diffuses preferentially along the [001] direction, i.e. along the

Ti and O_{br} rows. Furthermore, strand end-structures serve as preferred sites for Pt NP's following annealing at 800 K, where Pt NP's "extend" the strands towards the next step edge.

The decline of the Pt NP density as function of the annealing temperature differed for the four TiO_2 surfaces depending on the surface morphology and surface reduction state. These differences can be explained invoking a sintering model dominated by either particle diffusion/coalescence, or ripening.

Considering previous studies on the Pt/TiO_2 system, encapsulation of Pt NP's is expected to occur upon annealing the samples at 700 K and 800 K because of the SMSI effect. However, at the chosen experimental conditions in the present study no sign for particle encapsulation was observed.

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References

1. M. Bäumer and H.-J. Freund, *Prog. Surf. Sci.*, 1999, **61**, 127–198.
2. C. T. Campbell, *Surf. Sci. Rep.*, 1997, **27**, 1–111.
3. A. T. Bell, *Science*, 2003, **299**, 1688–1691.
4. M. Chen and D. W. Goodman, in *The Chemical Physics of Solid Surfaces*, ed. D. P. Woodruff, Elsevier B.V., 2007, vol. 12, pp. 201–269.
5. Q. Fu and T. Wagner, *Surf. Sci. Rep.*, 2007, **62**, 431–498.
6. G. A. Somorjai, H. Frei and J. Y. Park, *J. Am. Chem. Soc.*, 2009, **131**, 16589–16605.
7. R. M. Heck and R. J. Farrauto, *Appl. Catal. A.-Gen.*, 2001, **221**, 443–457.
8. B. A. A. L. van Setten, M. Makkee and J. A. Moulijn, *Catal. Rev.*, 2001, **43**, 489–564.
9. H. S. Gandhi, G. W. Graham and R. W. McCabe, *J. Catal.*, 2003, **216**, 433–442.
10. L. M. Petkovic, D. M. Ginosar, H. W. Rollins, K. C. Burch, P. J. Pinhero and H. H. Farrell, *Appl. Catal. A.-Gen.*, 2008, **338**, 27–36.

11. A. Russell and W. S. Epling, *Catal. Rev.*, 2011, **53**, 337–423.
12. A. Boubnov, S. Dahl, E. Johnson, A. P. Molina, S. B. Simonsen, F. M. Cano, S. Helveg, L. J. Lemus-Yegres and J.-D. Grunwaldt, *Appl. Catal. B.-Environ.*, 2012, **126**, 315–325.
13. P. Wynblatt and N. A. Gjostein, *Prog. Solid State Ch.*, 1975, **9**, 21–58.
14. C. H. Bartholomew, *Appl. Catal. A.-Gen.*, 2001, **212**, 17–60.
15. G. A. Somorjai, R. L. York, D. Butcher and J. Y. Park, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3500–3513.
16. C. T. Campbell and J. R. V. Sellers, *Faraday Discuss.*, 2013, **162**, 9–30.
17. S. B. Simonsen, I. Chorkendorff, S. Dahl, M. Skoglundh, J. Sehested and S. Helveg, *J. Am. Chem. Soc.*, 2010, **132**, 7968–7975.
18. S. B. Simonsen, I. Chorkendorff, S. Dahl, M. Skoglundh, J. Sehested and S. Helveg, *J. Catal.*, 2011, **281**, 147–155.
19. S. B. Simonsen, I. Chorkendorff, S. Dahl, M. Skoglundh, K. Meinander, T. N. Jensen, J. V. Lauritsen and S. Helveg, *J. Phys. Chem. C*, 2012, **116**, 5646–5653.
20. T. L. Thompson and J. T. Yates, *Chem. Rev.*, 2006, **106**, 4428–4453.
21. U. Diebold, *Surf. Sci. Rep.*, 2003, **48**, 53–229.
22. C. L. Pang, R. Lindsay and G. Thornton, *Chem. Rev.*, 2013, **113**, 3887–3948.
23. S. Wendt, R. Schaub, J. Matthiesen, E. K. Vestergaard, E. Wahlström, M. D. Rasmussen, P. Thostrup, L. M. Molina, E. Lægsgaard, I. Stensgaard, B. Hammer and F. Besenbacher, *Surf. Sci.*, 2005, **598**, 226–245.
24. Z. Dohnálek, I. Lyubinetsky and R. Rousseau, *Prog. Surf. Sci.*, 2010, **85**, 161–205.
25. M. A. Henderson, *Surf. Sci. Rep.*, 2011, **66**, 185–297.
26. S. Wendt, P. T. Sprunger, E. Lira, G. K. H. Madsen, Z. Li, J. Ø. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer and F. Besenbacher, *Science*, 2008, **320**, 1755–1759.
27. J. Matthiesen, J. Ø. Hansen, S. Wendt, E. Lira, R. Schaub, E. Lægsgaard, F. Besenbacher and B. Hammer, *Phys. Rev. Lett.*, 2009, **102**, 226101.
28. J. Matthiesen, S. Wendt, J. Ø. Hansen, G. K. H. Madsen, E. Lira, P. Galliker, E. K. Vestergaard, R. Schaub, E. Lægsgaard, B. Hammer and F. Besenbacher, *ACS Nano*, 2009, **3**, 517–526.
29. E. Lira, J. Ø. Hansen, P. Huo, R. Bechstein, P. Galliker, E. Lægsgaard, B. Hammer, S. Wendt and F. Besenbacher, *Surf. Sci.*, 2010, **604**, 1945–1960.
30. J. Ø. Hansen, P. Huo, U. Martinez, E. Lira, Y. Wei, R. Streber, E. Lægsgaard, B. Hammer, S. Wendt and F. Besenbacher, *Phys. Rev. Lett.*, 2011, **107**, 136102.
31. D. Matthey, J. G. Wang, S. Wendt, J. Matthiesen, R. Schaub, E. Lægsgaard, B. Hammer and F. Besenbacher, *Science*, 2007, **315**, 1692–1696.
32. J. Ø. Hansen, E. Lira, P. Galliker, J. Wang, P. T. Sprunger, Z. Li, E. Lægsgaard, S. Wendt, B. Hammer and F. Besenbacher, *J. Phys. Chem. C*, 2010, **114**, 16964–16972.
33. E. Lira, J. Ø. Hansen, L. R. Merte, P. T. Sprunger, Z. Li, F. Besenbacher and S. Wendt, *Top. Catal.*, 2013, **56**, 1460–1476.
34. S. Gan, Y. Liang, D. R. Baer and A. W. Grant, *Surf. Sci.*, 2001, **475**, 159–170.
35. A. Sasahara, C. L. Pang and H. Onishi, *J. Phys. Chem. B*, 2006, **110**, 13453–13457.
36. N. Isomura, X. Wu and Y. Watanabe, *J. Chem. Phys.*, 2009, **131**, 164707.
37. D.-e. Jiang, S. H. Overbury and S. Dai, *J. Phys. Chem. C*, 2012, **116**, 21880–21885.
38. D. Çakir and O. Gülseren, *J. Phys. Chem. C*, 2012, **116**, 5735–5746.
39. F. Behafarid and B. Roldan Cuenya, *Surf. Sci.*, 2012, **606**, 908–918.

40. F. Pesty, H. P. Steinrück and T. E. Madey, *Surf. Sci.*, 1995, **339**, 83–95.
41. O. Dulub, W. Hebenstreit and U. Diebold, *Phys. Rev. Lett.*, 2000, **84**, 3646–3649.
42. S. Bonanni, K. Aït-Mansour, H. Brune and W. Harbich, *ACS Catal.*, 2011, **2**, 385–389.
43. S. Bonanni, K. Aït-Mansour, W. Harbich and H. Brune, *J. Am. Chem. Soc.*, 2012, **134**, 3445–3450.
44. H. Iddir, M. M. Disko, S. Öğüt and N. D. Browning, *Micron*, 2005, **36**, 233–241.
45. H. Iddir, S. Öğüt, N. Browning and M. Disko, *Phys. Rev. B*, 2005, **72**, 081407.
46. H. Iddir, V. Komanicky, S. Öğüt, H. You and P. Zapol, *J. Phys. Chem. C*, 2007, **111**, 14782–14789.
47. O. Ozturk, J. B. Park, S. Ma, J. S. Ratliff, J. Zhou, D. R. Mullins and D. A. Chen, *Surf. Sci.*, 2007, **601**, 3099–3113.
48. J. B. Park, S. F. Conner and D. A. Chen, *J. Phys. Chem. C*, 2008, **112**, 5490–5500.
49. S. Bonanni, K. Aït-Mansour, W. Harbich and H. Brune, *J. Am. Chem. Soc.*, 2014, **136**, 8702–8707.
50. S. J. Tauster, S. C. Fung and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170–175.
51. S. J. Tauster, *Accounts Chem. Res.*, 1987, **20**, 389–394.
52. A. Berkó, I. Ulrych and K. C. Prince, *J. Phys. Chem. B*, 1998, **102**, 3379–3386.
53. A. Berkó, J. Szökő and F. Solymosi, *Surf. Sci.*, 2003, **532-535**, 390–395.
54. M. Bowker, P. Stone, P. Morrall, R. Smith, R. Bennett, N. Perkins, R. Kvon, C. Pang, E. Fourre and M. Hall, *J. Catal.*, 2005, **234**, 172–181.
55. Z. Qin, M. Lewandowski, Y. Sun, S. Shaikhutdinov and H. Freund, *J. Phys. Chem. C*, 2008, **112**, 10209–10213.
56. A. Berkó, O. Hakkel, J. Szökő and F. Solymosi, *Surf. Sci.*, 2002, **507-510**, 643–648.
57. R. Bechstein, H. Kristoffersen, L. Vilhelmsen, F. Rieboldt, J. Stausholm-Møller, S. Wendt, B. Hammer and F. Besenbacher, *Phys. Rev. Lett.*, 2012, **108**, 236103.
58. F. Rieboldt, R. Bechstein, F. Besenbacher and S. Wendt, *J. Phys. Chem. C*, 2014, **118**, 3620–3628.
59. E. Lira, S. Wendt, P. Huo, J. Ø. Hansen, R. Streber, S. Porsgaard, Y. Wei, R. Bechstein, E. Lægsgaard and F. Besenbacher, *J. Am. Chem. Soc.*, 2011, **133**, 6529–6532.
60. E. Lira, P. Huo, J. Ø. Hansen, F. Rieboldt, R. Bechstein, Y. Wei, R. Streber, S. Porsgaard, Z. Li, E. Lægsgaard, S. Wendt and F. Besenbacher, *Catal. Today*, 2012, **182**, 25–38.
61. D. Briggs and M. P. Seah, *Practical Surface Analysis*, 2 edn., Wiley, New York, 1990.
62. K. D. Schierbaum, S. Fischer, M. C. Torquemada, J. L. de Segovia, E. Román and J. A. Martín-Gago, *Surf. Sci.*, 1996, **345**, 261–273.
63. U. Martinez, L. Vilhelmsen, H. Kristoffersen, J. Stausholm-Møller and B. Hammer, *Phys. Rev. B*, 2011, **84**, 205434.
64. U. Martinez, J. Ø. Hansen, E. Lira, H. H. Kristoffersen, P. Huo, R. Bechstein, E. Lægsgaard, F. Besenbacher, B. Hammer and S. Wendt, *Phys. Rev. Lett.*, 2012, **109**, 155501.
65. H. H. Kristoffersen, J. Ø. Hansen, U. Martinez, Y. Y. Wei, J. Matthiesen, R. Streber, R. Bechstein, E. Lægsgaard, F. Besenbacher, B. Hammer and S. Wendt, *Phys. Rev. Lett.*, 2013, **110**, 146101.
66. T. P. Hardcastle, C. R. Seabourne, R. M. D. Brydson, K. J. T. Livi and A. J. Scott, *J. Phys. Chem. C*, 2013, **117**, 23766–23780.
67. J. Stausholm-Møller, H. H. Kristoffersen, U. Martinez and B. Hammer, *J. Chem. Phys.*, 2013, **139**, 234704.

68. R. L. Kurtz, R. Stockbauer, T. E. Madey, E. Román and J. L. De Segovia, *Surf. Sci.*, 1989, **218**, 178–200.

Figure Captions:

Fig. 1. Ball model of a TiO_2 (110) surface, illustrating the surface structure and the creation of vicinal surfaces. Slightly miss-cutting in $\left[1\bar{1}0\right]$ direction leads to surfaces with high densities of [001] step edges, i.e. TiO_2 (870). Miss-cutting in [001] direction leads to surfaces with high densities of $\left[1\bar{1}1\right]$ step edges, i.e. TiO_2 (771). Step edges, strands, surface atoms and point defects are indicated.

Fig. 2. (a)-(c) STM images (60 nm × 60 nm; insets: 10 nm × 10 nm) of clean TiO_2 (110), (870) and (771), respectively. Strands, which dominate the TiO_2 (771) surface, occasionally also appeared on the other two surfaces (black ellipses). The empty state STM images were acquired at 90–110 K in the constant current mode (~1.2 V, 0.1 nA). (d)-(f) Corresponding VB spectra (UPS He I), measured after ~40 cycles of sample preparation. The gap state (GS) is enlarged by a factor of 50. The dashed lines correspond to the GS's of the other two surfaces, respectively, and assist a direct comparison. Positions of the valence band maximum (VBM) and the Fermi energy (E_F) are indicated.

Fig. 3. STM images (60 nm × 60 nm) of the HR-TiO_2 (110) surface and the vicinal TiO_2 (870) and (771) surfaces following evaporation of ~0.1 ML Pt at RT [(a)-(c)], and subsequent vacuum-annealing for 5 min at 600 K [(d)-(f)], 700 K [(g)-(i)] and 800 K [(k)-(m)], respectively. Note that the annealing experiments were conducted as separate experiments for each annealing temperature. In (k)-(m), black squares mark three Pt NP's with heights larger than 0.65 nm [two atomic layers of TiO_2 (110)].

Fig. 4. STM images (60 nm × 60 nm) of the HR-TiO_2 (110) (left column) and the SR-TiO_2 (110) (right column) surfaces, obtained following evaporation of ~0.1 ML Pt at RT [(a),(b)], and subsequent annealing for 5 min at 600 K [(c),(d)], 700 K [(e),(f)] and 800 K [(g),(h)], respectively. Note that the annealing experiments were conducted as separate experiments for each temperature using the two

described $TiO_2(110)$ samples. The dark lines in [001] direction occasionally appearing in the STM images of the HR-TiO_2 surface are electronic artefacts that have been observed before.

Fig. 5. VB spectra (UPS He I) of HR- and SR-TiO_2 surfaces. The GS is enlarged by a factor of 50. The different integrated areas of the GS's, i.e. the amounts of Ti^{3+} excess charge, indicate the different surface reduction states of these two samples. Positions of VBM and E_F are indicated.

Fig. 6. STM images (23 nm × 23 nm) of (a) clean TiO_2 (771) and (b) after evaporation of ~0.1 ML Pt at RT and subsequent annealing for 5 min at 800 K. Symbols in (b) indicate Pt NP's at $\left[1\bar{1}1\right]$ step edges (circle), on top of the periodic strand centre-parts (diamond) and at strand end-structures (square), respectively.

Fig. 7. Densities of Pt NP's on various TiO_2 (110) surfaces, obtained after Pt evaporation at RT and following annealing at 600 K, 700 K and 800 K, respectively. For each data point, six STM images (60 nm × 60 nm) were analysed. The error bars were calculated using the standard deviation for mean values.

Fig. 8. (a) Pt NP densities and (b) relative Pt NP densities on terraces (blue), step edges (yellow) and strands (grey) on various TiO_2 surfaces, obtained after Pt evaporation at RT and subsequent annealing at 600 K, 700 K and 800 K, respectively. For each column, six STM images (60 nm × 60 nm) were analysed.