Formation and stabilization of nano-sized Pt clusters on TiO_2 Surfaces

by

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Introduction:

- Microchemical systems are generally optimized in relation to transport of critical chemical components to and from the reaction sites
- In the absence of transport limitations, surface reaction rates for catalytic systems may become the rate limiting process
- The efficiency and reliability of microsystems can be greatly enhanced by nanodimensional components with artificially tailored properties
- Nanodimensional information about surfaces and supported metal clusters is crucial for development of a new generation of catalyst for microchemical systems

Objectives:

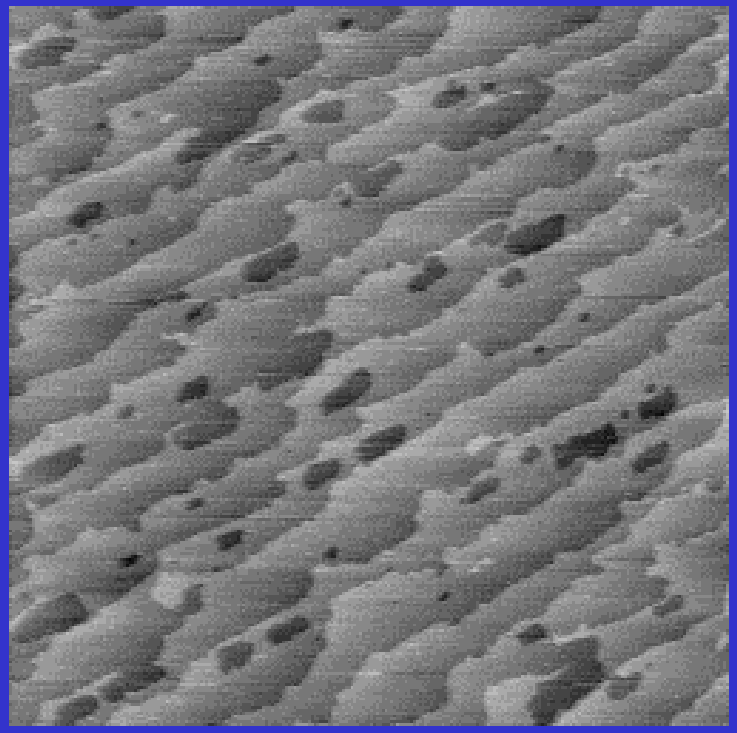
- Develop methods to create surfaces with increased functionality for improved catalytical efficiency
- Produce self-assembled nano-sized metal-cluster arrays for a next generation of catalyst
- Examine the formation and stability of platinum nanoclusters on rutile (110) and anatase (001) surfaces

Outline

- Pt nanoclusters on rutile TiO_2 surfaces
  - Randomly distributed on (1x1) surface
  - Attached to the step edges on (1x2) surface
- Pt nanoclusters deposited on anatase TiO_2 surface
  - Preferentially decorated at the step edges

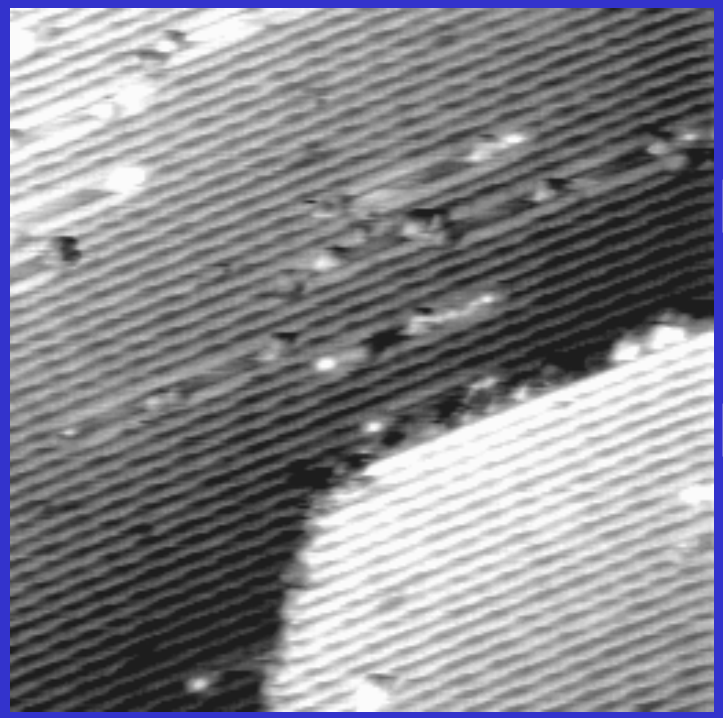
Surface Preparation by Oxygen Plasma Treatment

- Degreased in organic solvents followed by gentel Ar sputtering
- Exposed to oxygen plasma at above 500 ^{o}C
- Annealing at 500 ^{o}C in UHV to produce (1x1)
- Further sputtering and annealing to create (1x2)



0µm 2µm

Surface Structures of TiO_2(110)- (1x1) and (1x2)

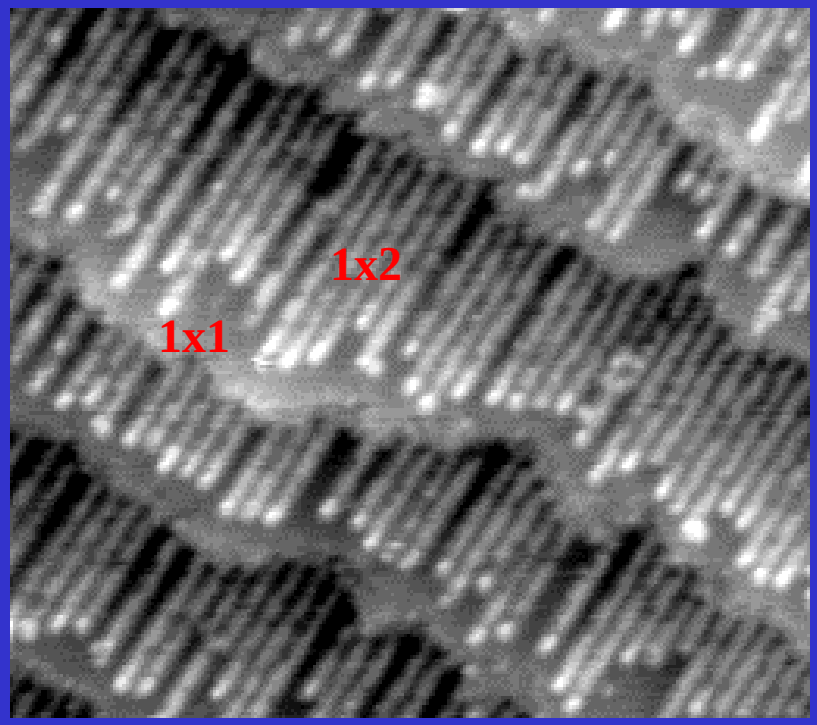


250 Å

1x1

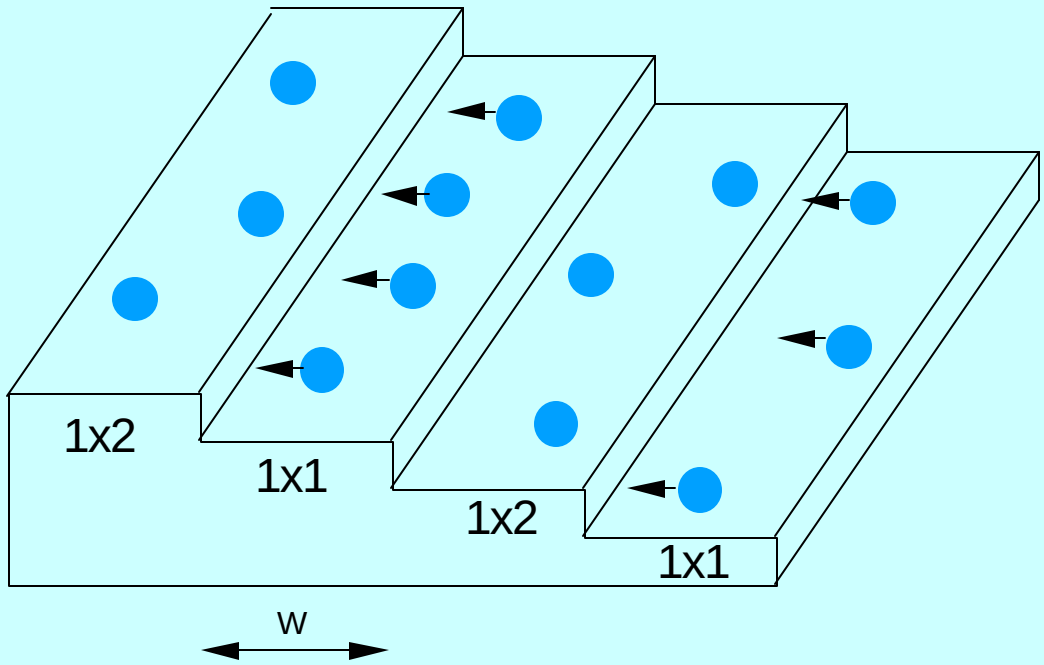
[1$\bar{1}$0]

[001]



400 Å

1x2

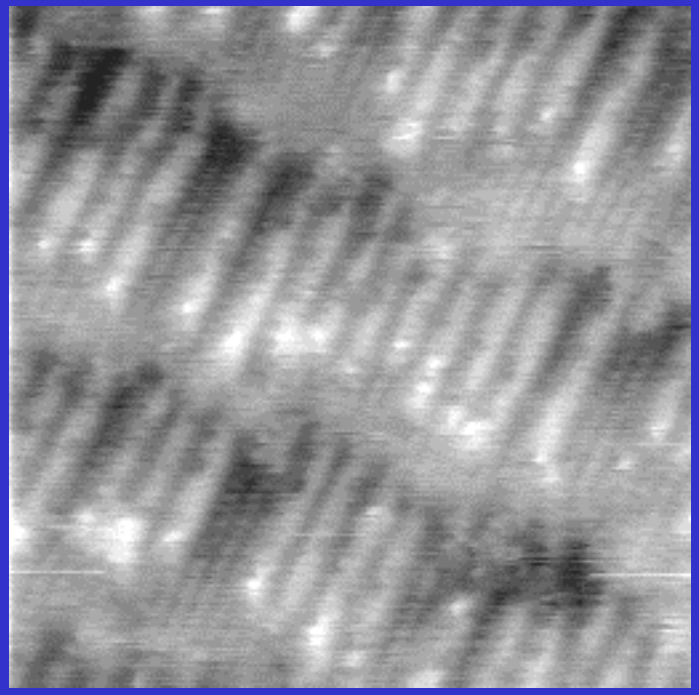


To observe different interactions of Pt with Rutile (1x1) and (1x2):

1) Co-existence of (1x1) and (1x2) phases

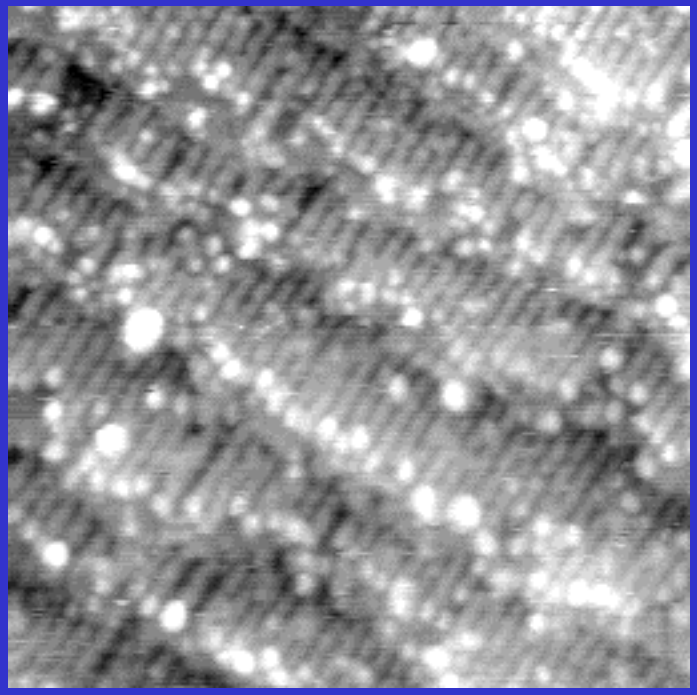
2) Diffusion length > Terrace width (W)

Pt Nanoclusters Self-assembled along the Step Edges on (1x2)



0 Å 200 Å

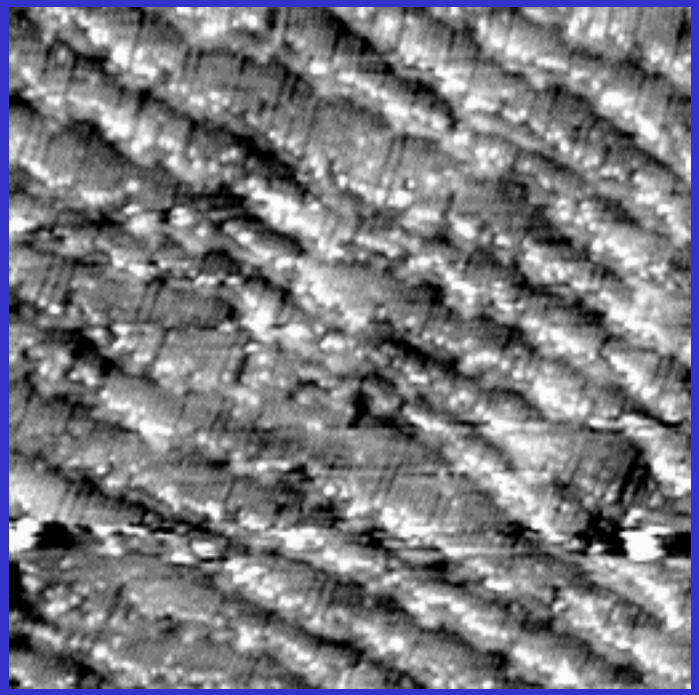
Before Pt deposition



0 Å 400 Å

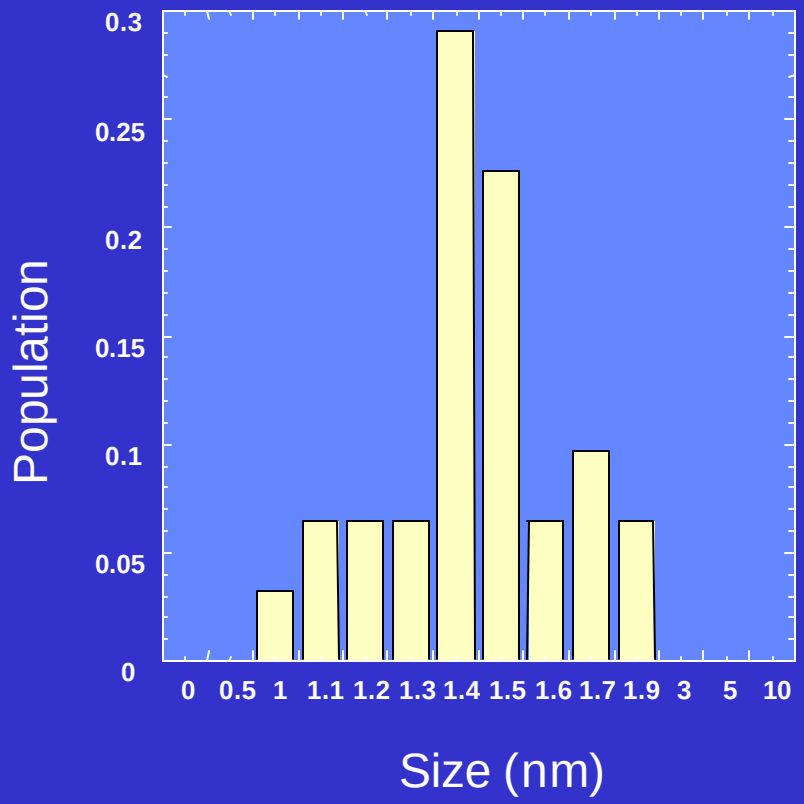
After Pt deposition

Selective Deposition of Pt on TiO_2(110)



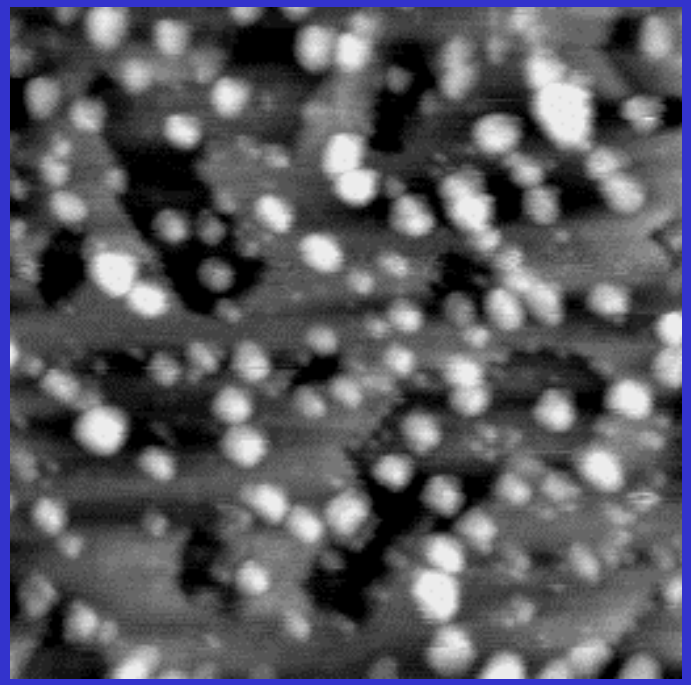
0 Å 1000 Å

Size distribution of Pt nanoclusters



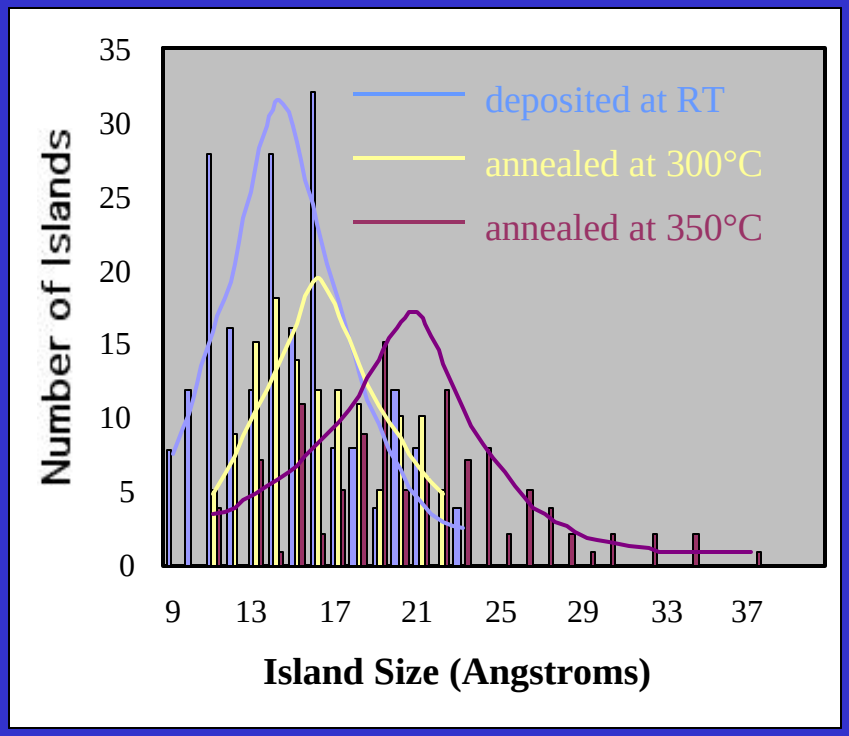
Average size (Å)	14
FWHM (Å)	5

Formation of Pt Nanoclusters on Rutile (1x1)



0 Å 500 Å

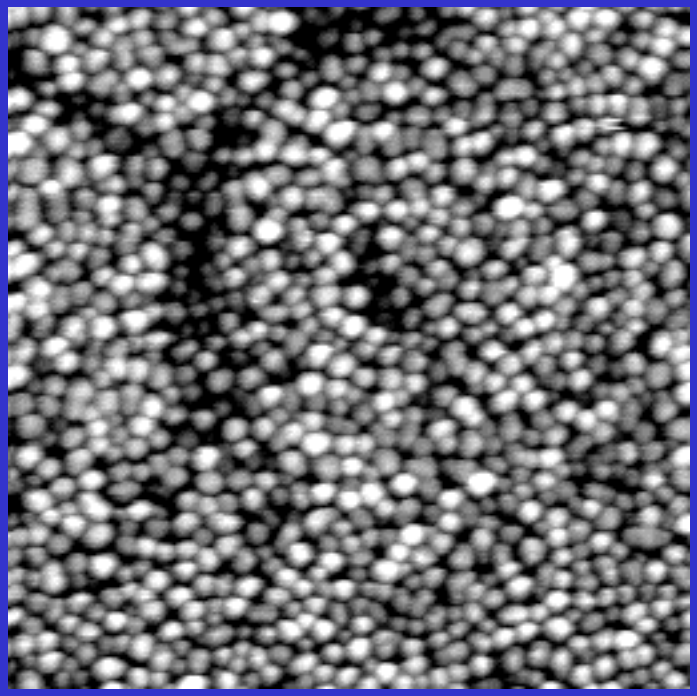
Pt clusters randomly distribute on the surface after 0.5 ML of Pt deposition



The size of Pt clusters varies with annealing temperatures

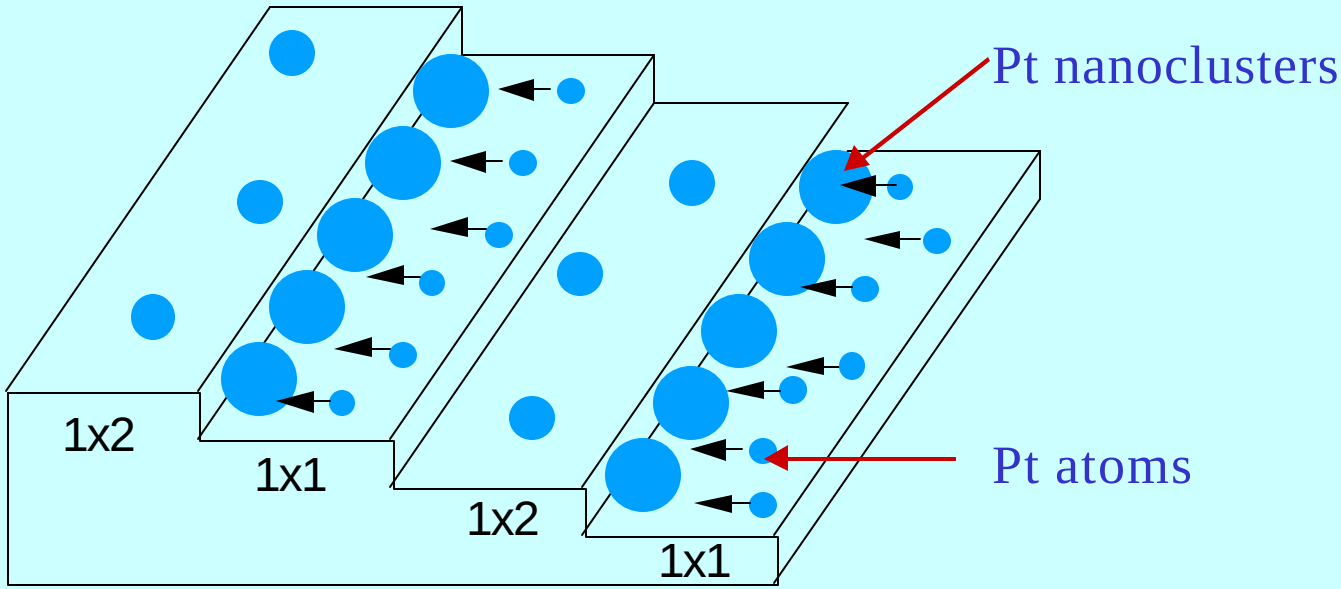
Temperature (K)	300	600	650
Average size (Å)	14	16	20
FWHM (Å)	10	5	8

Morphology of TiO_2(110) After 5 ML of Pt Deposition



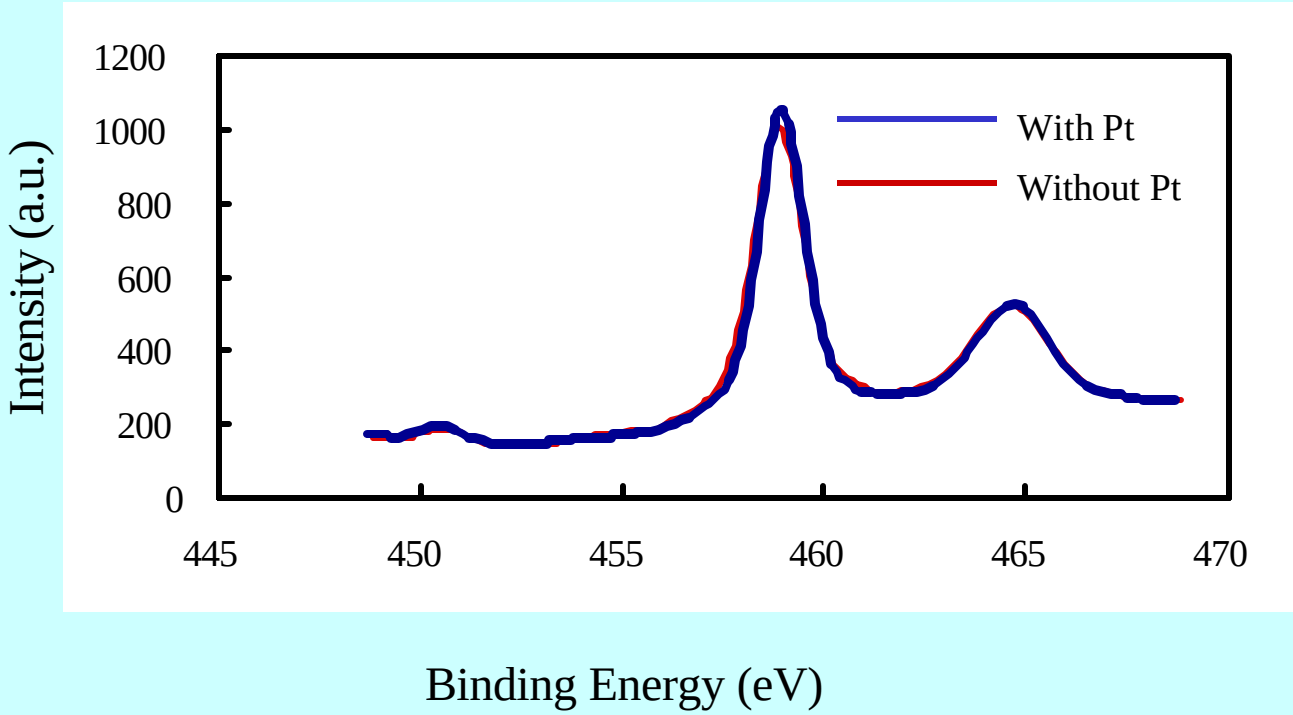
Ring structure indicates the close packing of Pt clusters

Stronger Interaction of Pt with (1x2) Step Edges Results in Formation of Self-organized Pt nanoclusters Strings

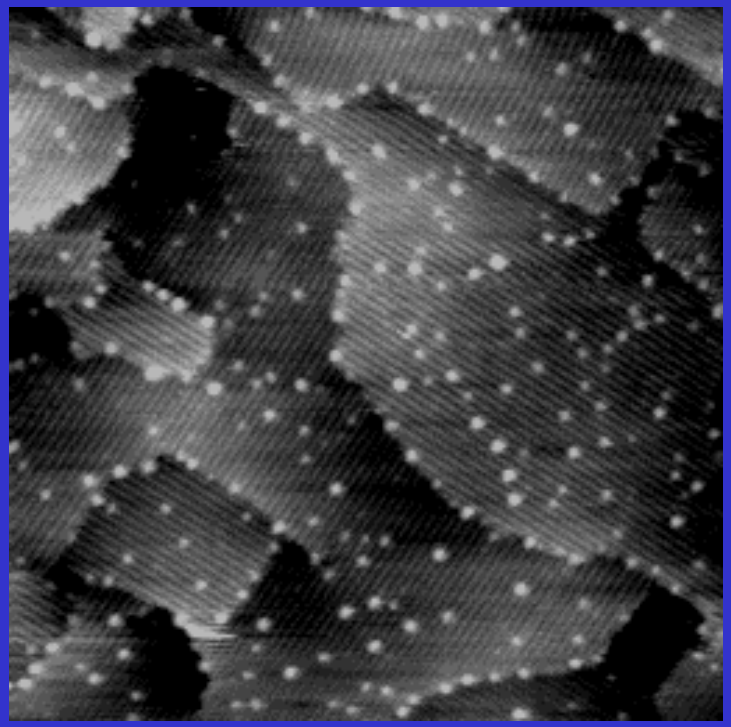


Diffusion Length > Terrace Width

XPS of a TiO_2(110) (1x2) With and Without Pt Deposition

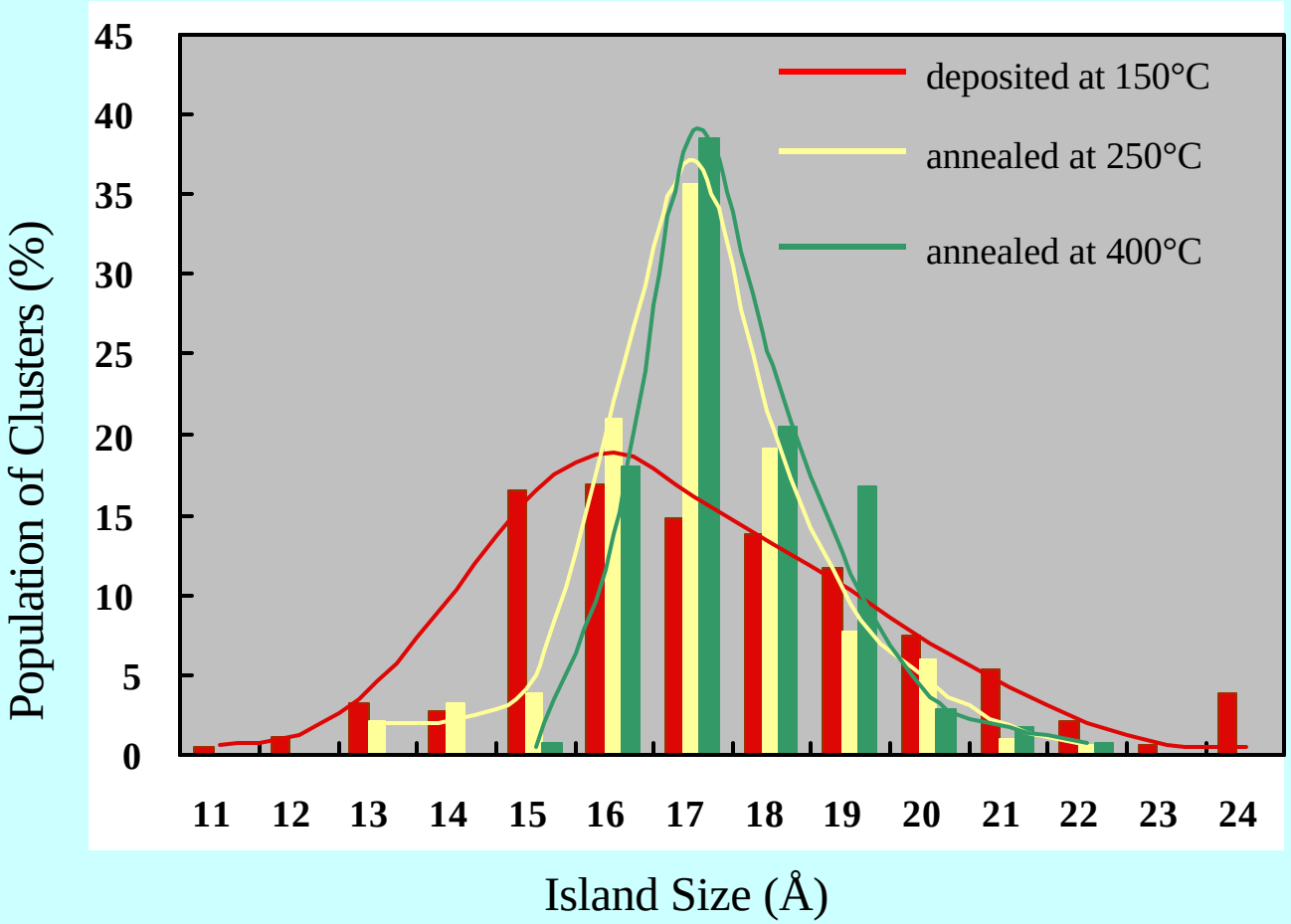


Pt Nanoclusters Preferentially Attach to Step Edges on the Anatase (001)-(4x1) Surface



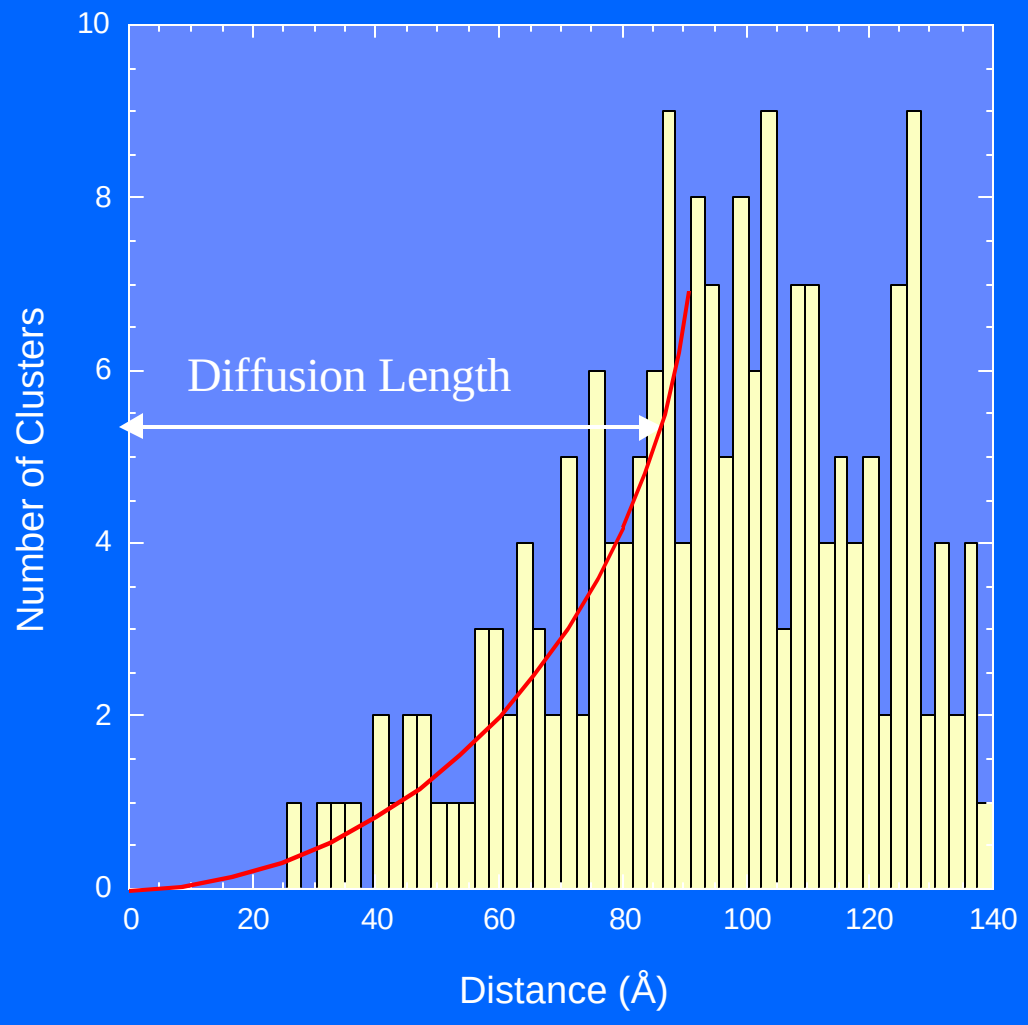
0 Å 1200 Å

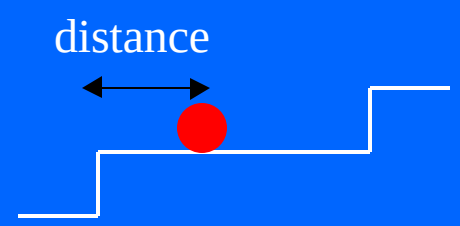
Size Distribution of Pt Clusters on Anatase (001) Surface



Temperature (°C)	150	250	400
Average size(Å)	15.2	17.3	17.7
FWHM(Å)5	2.3	2.2	

Displacement Distribution of Pt Clusters After Annealing at 450°C





Diffusion length (450°C): 84 Å

Conclusions

- A comparative study has been conducted on the formation of Pt nanoclusters on rutile [(1x1) and (1x2)] and anatase surfaces. Results show that Pt exhibits stronger interaction with rutile (1x2) and anatase surfaces, which in turn results in higher thermal stability of Pt clusters on these surfaces.

- We have successfully formed organized strings of Pt nanoclusters on rutile TiO_2 (110)-(1x2) surface through self-assembly. This approach may lead to the formation of multi-component systems on TiO_2 surfaces via self-assembly.

- MBE grown anatase TiO_2 (001) is terminated by a (4x1) structure, on which Pt clusters preferentially decorate at the step edges. The diffusion length of Pt on the anatase (4x1) surface is determined to be 84 Å at 450°C.