Carbon removal from EUV mirror cap layers: model studies

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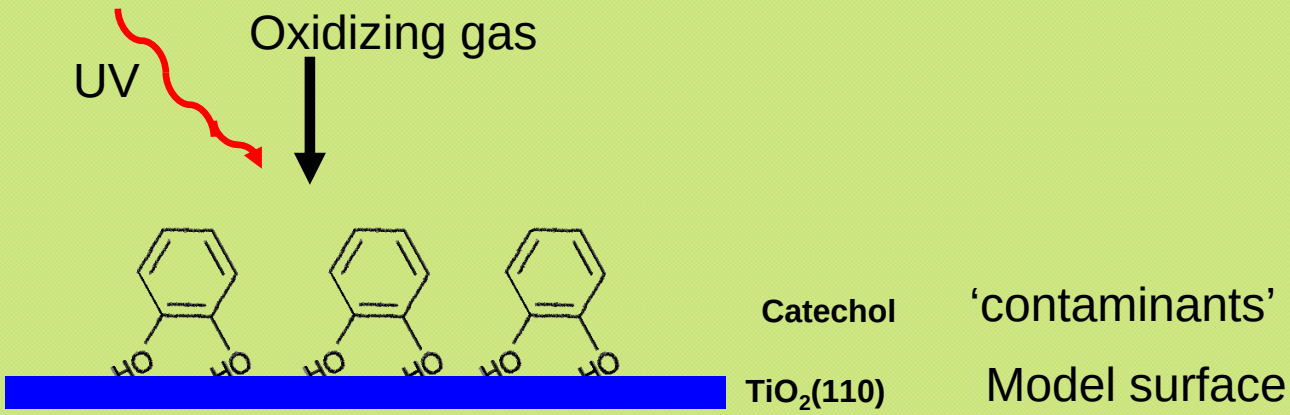
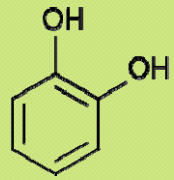
Overall Objective:

Through surface science investigations of a model surface (TiO_2(110) single crystal), covered with model 'contaminants', provide insights into uv-induced surface chemistry relevant to remediation strategies.



Outline:

1. Removal of a model contaminant (one monolayer (ML) of catechol) under uv-irradation. Influence of different parameters (type of gas, gas pressure, dosing scheme, temperature, etc.)



2. Growth and uv-induced removal of thicker C layers(>1 ML)

Photochemical removal of a monolayer of catechol

Experimental details

- **Photons:** Excimer laser - *KrF (5 eV)*, power (0.24 J x 10 Hz=*2.4 W*). Typical irradiation time: -about *3 hours* total, in *various gas backgrounds*. Different dosing configuration (direct dosing, backfill)

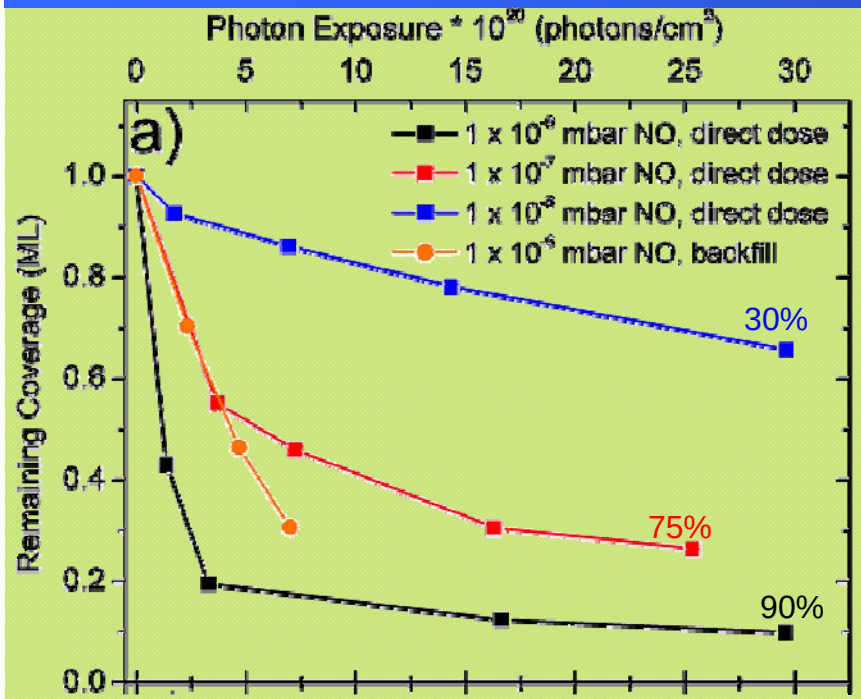
- **Sample:** Freshly prepared TiO_2(110) single crystal with catechol dosed (background dosing) from vapor above purified powder, normally start with a full monolayer.

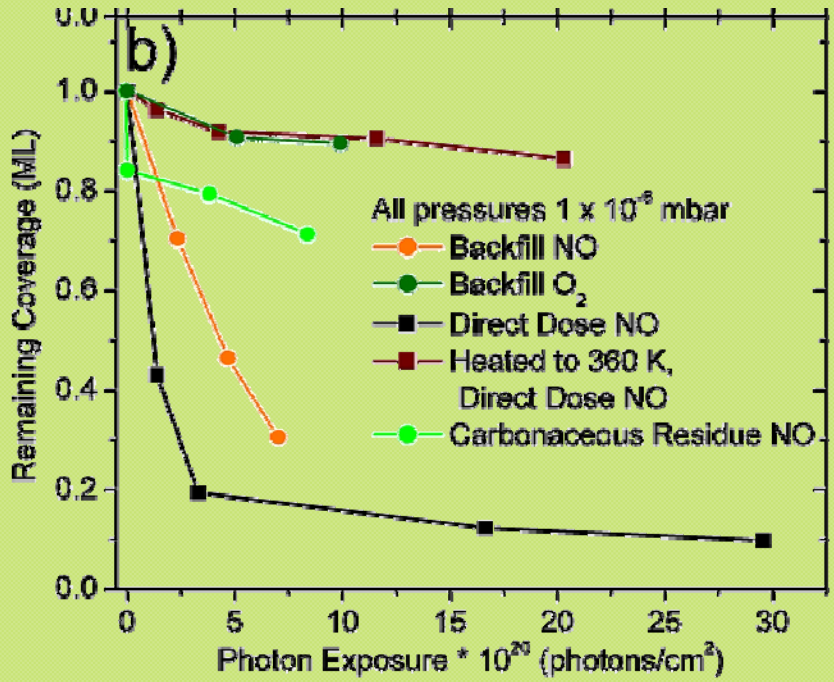
- **XPS:** (Mg K alpha) integrated peaks after BG subtraction, coverage (in fractional monolayers) evaluated from XPS signals taking into account published sensitivity factors.

$$C(\%) = \frac{C1s/S_C}{C1s/S_C + O1s/S_O + Ti2p/S_{Ti}}$$

- Additional studies (UPS, STM, DFT, IRAS, etc.) for further, more fundamental insights

Removal of Catechol in NO background:



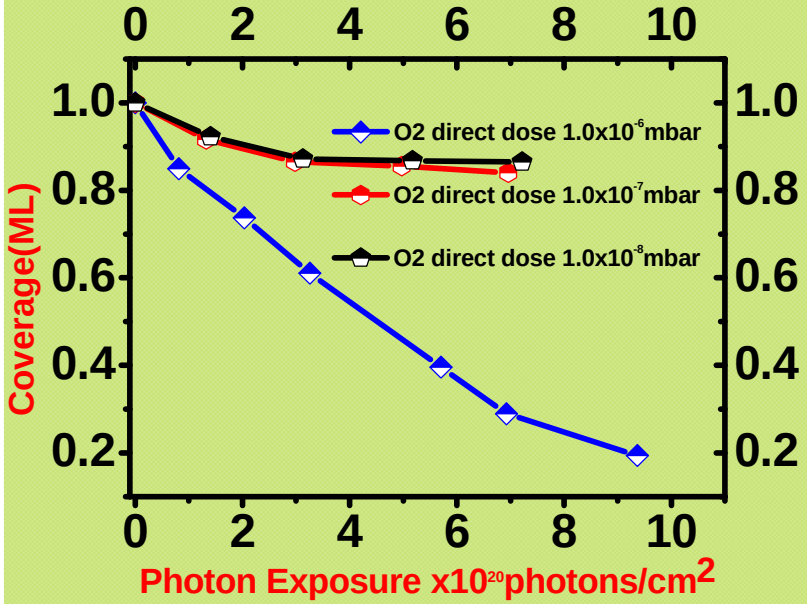


- Direct dosing scheme, enhance Carbon removal efficiency~ x10
- Strong function of pressure

variation of gas, C layer, sample temperature, dosing scheme

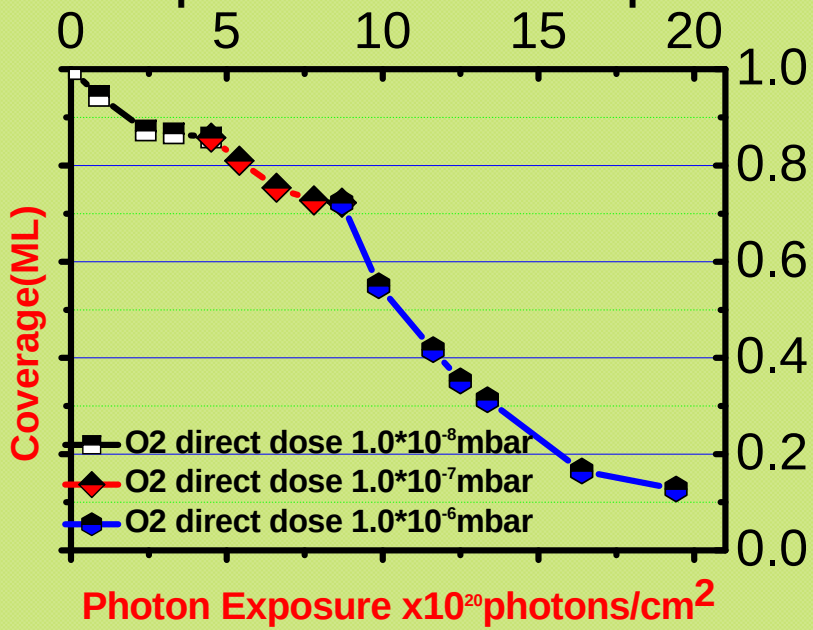
- Heating the sample reduces the efficiency of photo-induced C removal!

Removal of Catechol in O_2 background:



- Not a strong function of pressure in low pressure.
- Low efficiency compare to NO

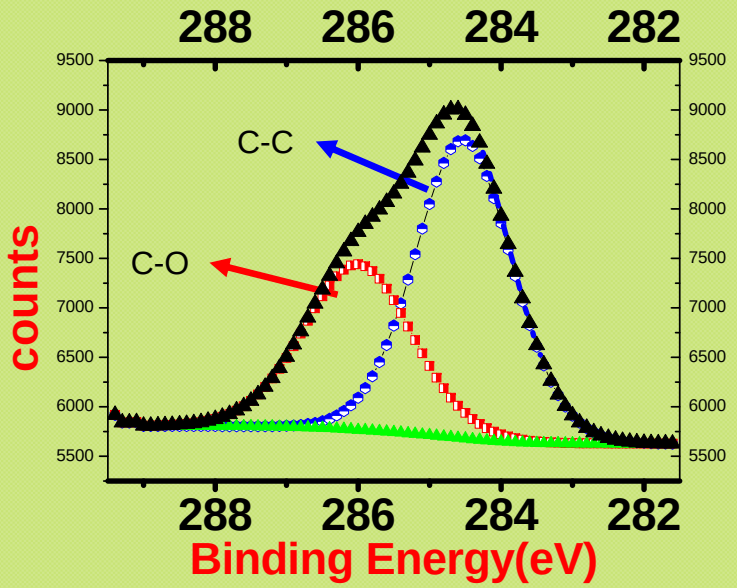
- **Hypothesis: Does the C layer change upon irradation, leading to a harder-to-remove overlayer?**
- **Test: Continuous photon irradiation, with step-wise increase of O2 pressure**



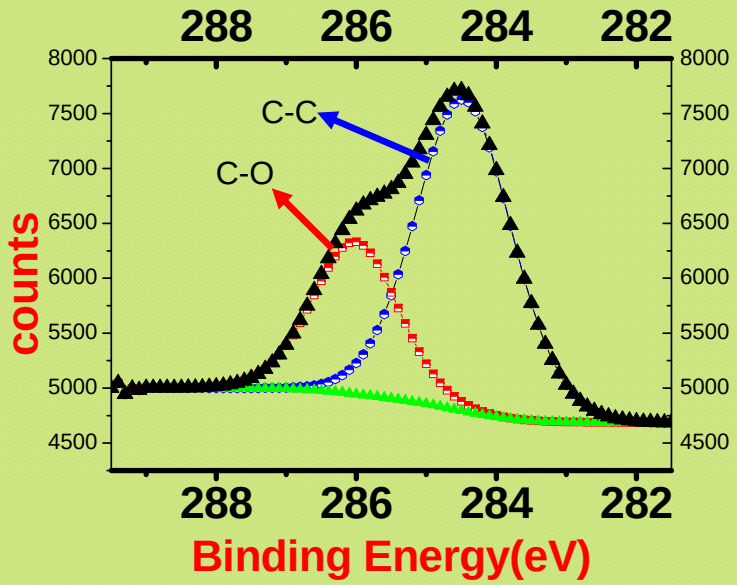
- O_2 pressure increase leads to increase of C removal rate, independent of history

Removal of Catechol in N_2O background:

Before N_2O exposure

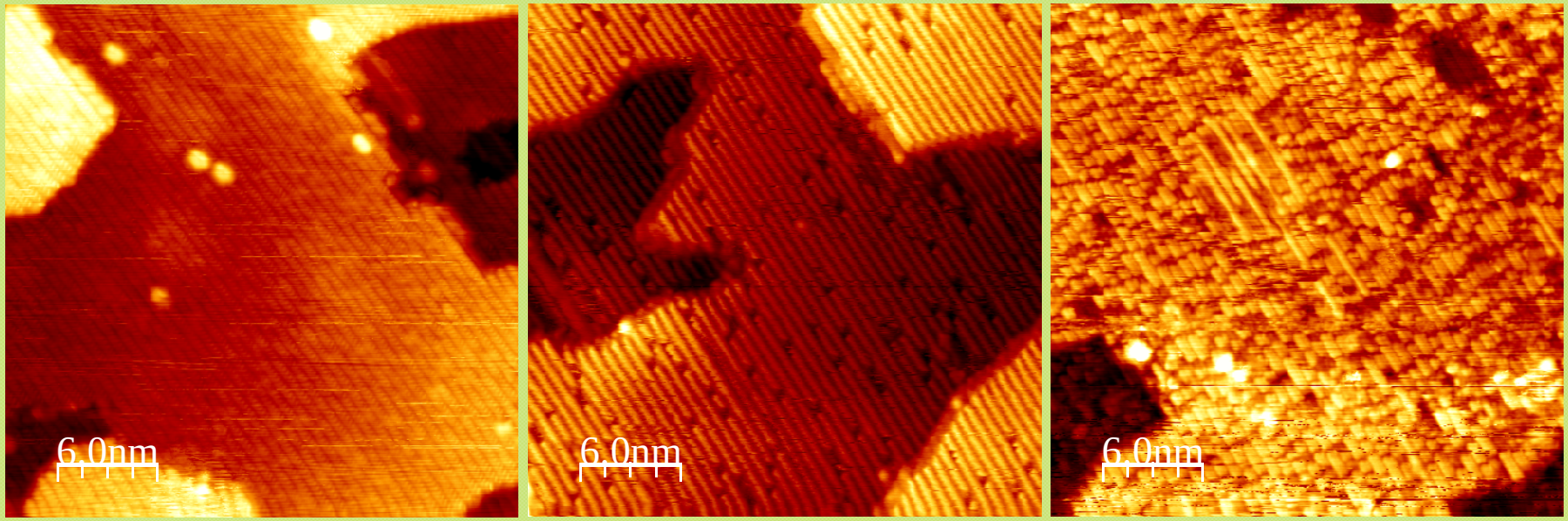


After N_2O exposure



- UV irradiation in N_2O, P=1x10^{-6} mbar with direct dosing configuration, (gas was checked for purity) 90 min, flux = 100 mJ (~1.5 x10^{20} photons/cm^2)
- XPS C1s signal unchanged in shape and intensity, no catechol removal observed.

STM of TiO_2(110) dosed with NO

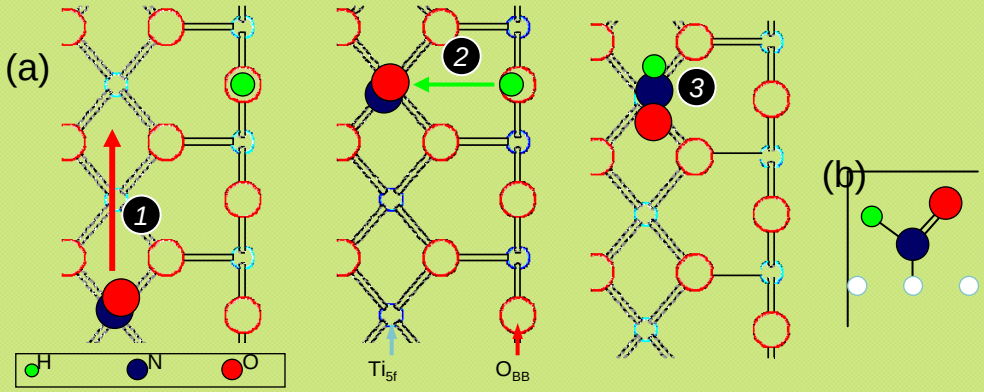


Clean TiO_2(110)-1×1 | Small Coverage | High Coverage

- NO adsorbs at the surface at room temperature
- Results are in contrast to TPD measurements by Yates et al.[1] on stoichiometric surfaces (NO physisorbs, desorbs around 170 K)
- STM, UPS, and XPS results indicate that NO interacts with surface hydroxyls

1. Sorescu et al., J. Phys. Chem. B 104 (18) (2000) 4408

Model: interaction of NO with surface hydroxyls



Proposed reaction model of NO with the hydroxylated TiO_2(110)-1×1 surface:

1. **NO molecule adsorbs weakly and diffuses along a Ti^{4+} row;**
2. **It passes along a hydroxylated surface O atom**
3. **the H combines with NO and an HNO intermediate* is formed.**

(*Formation/identification of the intermediate species is currently being tested with vibrational studies)

Hypothesis from previous studies:

- The oxidizing gas must be adsorbed at the TiO_2(110) surface for effective photocatalytic removal of the catechol layer

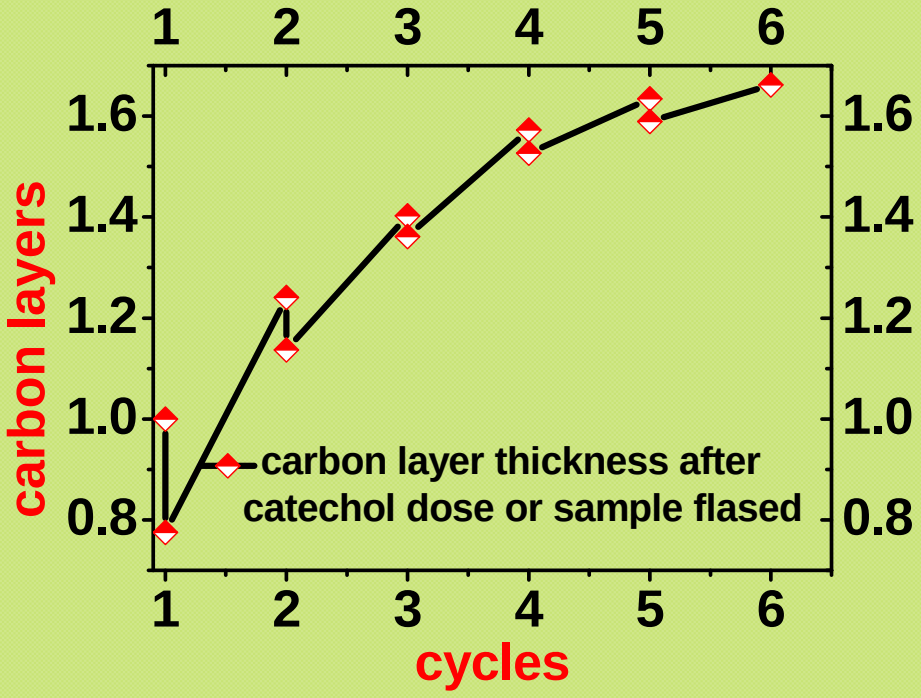
- NO, through interaction with surface hydroxyls, adsorbs more strongly than O_2

- Probably, N_2O does not adsorb at room temperature.
  Is it possible to activate N_2O adsorption, e.g., through co-dosing with water?

Thicker Carbon Layer:

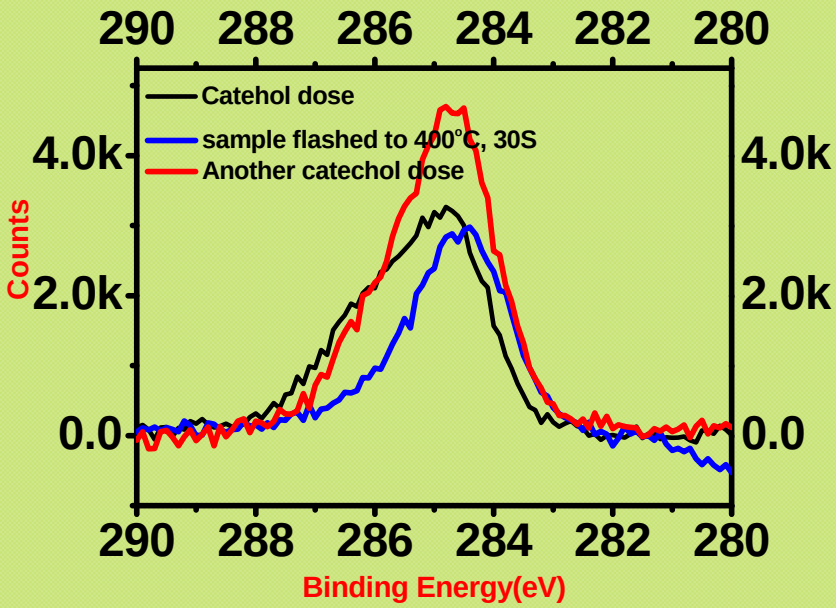
Effect of UV Irradiation in Oxidizing Gases

Growth of a thicker carbon layer: catechol dosing & flashing

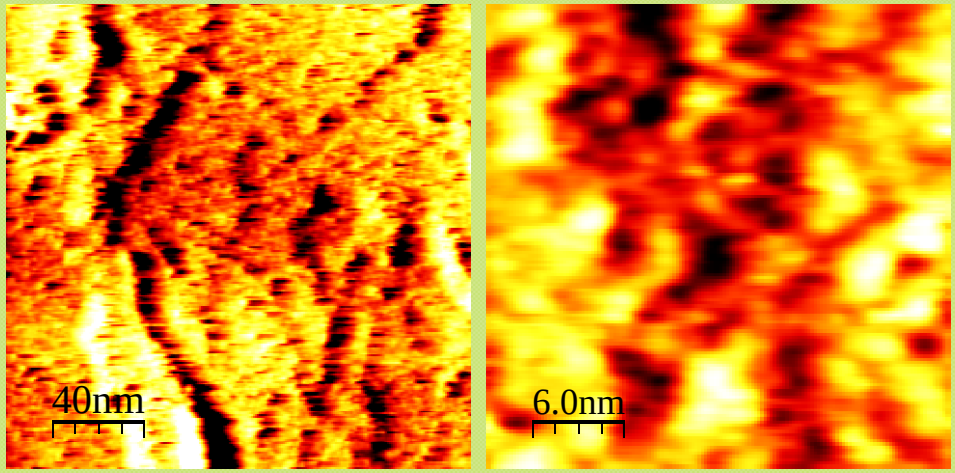


- In each cycle, the sample was exposed to a saturation coverage of catechol and then flashed to 400ºC for 30 s.
- After the film reaches a thickness of 1.6 monolayers of C, <u>no additional catechol adsorbs</u>, and the film thickness cannot be increased

XPS & STM result of thicker carbon layers



- After the sample was annealed, the C-O shoulder is missing

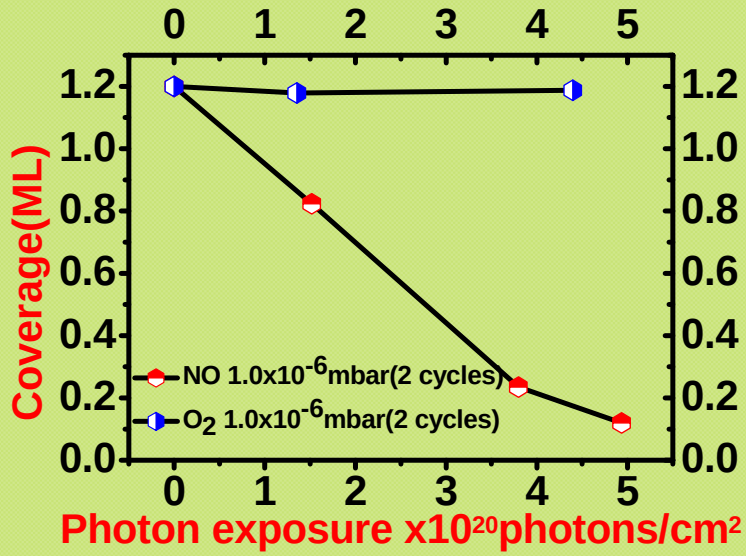


200nmx200nm, 0.4nA,1.5V 30nmx30nm, 0.5nA 1.1V

- Topography of the thicker carbon layers.

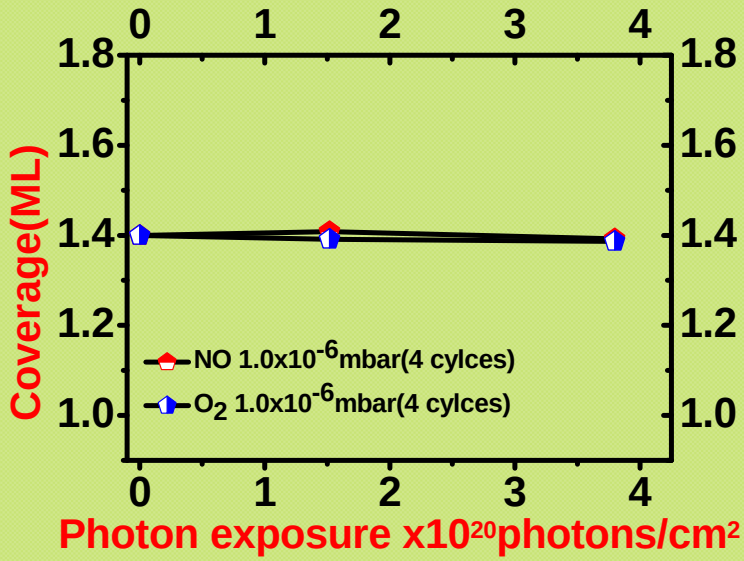
UV irradiation of thick carbon layers:

Starting point: 1.2 ML of C (2 cycles)



- irradation in NO removes the thicker C layer
- irradiation in O_2 shows no sign of C removal

Starting point: 1.4 ML of C (4 cycles)



- For a thicker film, irradiation shows no C removal in NO nor O_2.
- Film <u>too inert</u> to for oxidizing gases to stick?

Summary

- UV irradiation (5 eV) in a background of oxidizing gases is efficient in oxidizing and removing a monolayer of catechol from TiO_2(110)
- Indications that it is the photo-activation of the TiO_2 itself rather than the photoactivation of the adsorbate (no C-removal on thin Al_2O_3 film)
- Works only when an oxidizing gas is present: O_2 or NO.
- Strong function of pressure (the higher the pressure, the higher the removal rate for NO, somewhat different for O_2 background)
- Increase of temperature *reduces* C removal rate
- UV irradiation in N_2O shown *no effect*
- NO adsorbs on TiO_2 at room temperature (potentially through the interaction with surface hydroxyls)
- Thicker C layer (graphitic) are much harder to remove
- Hypothesis: the oxidizing gas must be adsorbed to the surface for the oxidation /removal process to happen. the removal rate for NO, somewhat different for O_2 background

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Thank You!