Characterization of graphene decorated with TiO_2 grown by atomic layer deposition (ALD)

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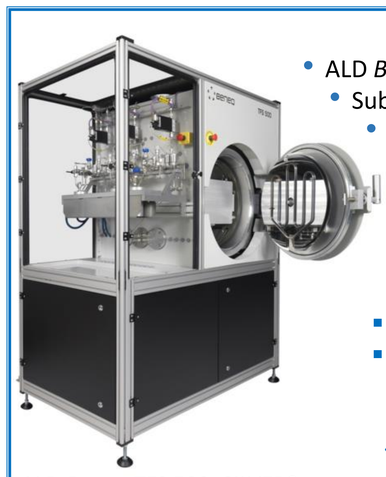
The great potentialities of graphene can be enhanced by means of the functionalization of its surface, which makes it suitable for different application fields. For this aim, the changes in electronic structure of graphene after the deposition of TiO_2 and the influence of graphene on TiO_2 photocatalytic activity were studied. Films with different thicknesses of TiO_2 were grown on graphene films by atomic layer deposition (ALD) at 200 °C using water (H_2O) and titanium tetrachloride ($TiCl_4$) as precursors. The changes in electronic structure of graphene were investigated by means of Raman spectroscopy and the TiO_2 stoichiometry was studied by X-ray photoelectron spectroscopy (XPS). The photocatalytic activity of TiO_2/Graphene hybrid material was tested under a UV-Visible irradiation (generated by a solar simulator) using UV-Visible spectrophotometry.

The results indicate that inhomogeneity and intrinsic strain effects are present within the same sample. A study on undecorated graphene showed pre-existent strain due to the mismatch between graphene film and the underlying substrate, while nonintentional self-doping is caused by the presence of charged impurities on the substrate itself. The deposition of TiO_2 films with thickness ≤ 10 nm led graphene to be p-doped, while strain becomes the dominant effect increasing film thickness. Oxygen vacancies, detected by XPS, decrease exponentially increasing the thickness of the TiO_2 films to reach a stoichiometric O/Ti atomic ratio above 10 nm thickness, where anatase phase signal appeared. The combination of TiO_2 and graphene enhanced the efficiency of electron-hole separation of TiO_2 under UV-Visible light, which gives rise to a higher photocatalytic activity tested for methyl red molecule degradation, leading TiO_2/Graphene hybrid material to be successfully employed for the photodegradation of pollutants and water purification.



Deposition details

- ALD *Beneq TFS 500nSILVER®* (figure)
- Substrate: Graphene film (Graphenea)
- TiO_2 Precursors: H_2O and TCl_4
- Processing temperature 200°C
- No. of ALD cycles: 7, 15, 30, 75, 105, 150, 375, 750, 1125.

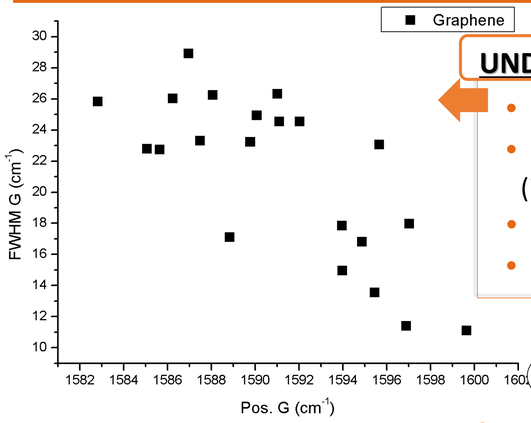
Raman characterization

- HORIBA LabRAM *Aramis*
- Red laser: λ= 632,8 nm (1,96 eV)

XPS characterization

- Scienta ESCA 200
- Monochromatic Al Kα X-ray source (1486,6 eV)

RAMAN CHARACTERIZATION

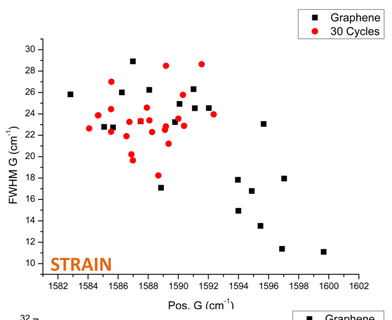


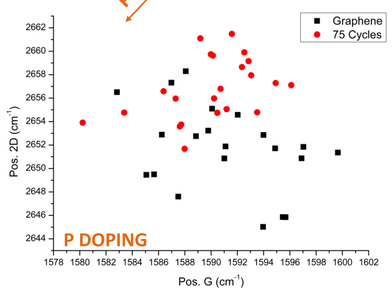
UNDOPED GRAPHENE FILM

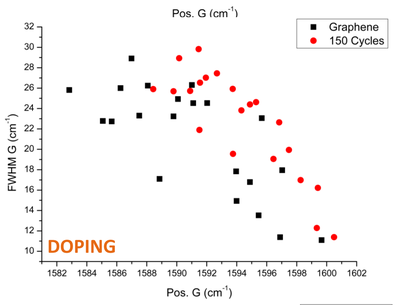
- **Non**-uniform
- Self-doping (induced by the substrate)
- Pre-existent strain
- Structural disorder

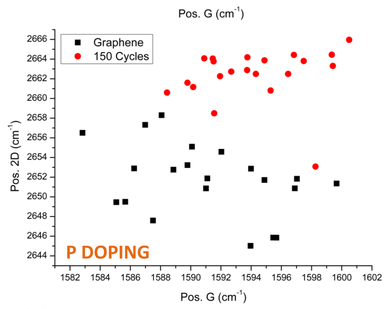
…AFTER TiO_2 DEPOSITION (by ALD)…

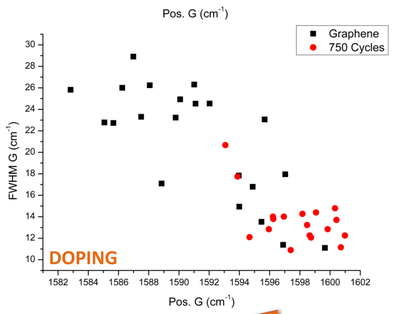
FWHM G vs Pos. G | Pos. 2D vs Pos. G | Raman of TiO_2

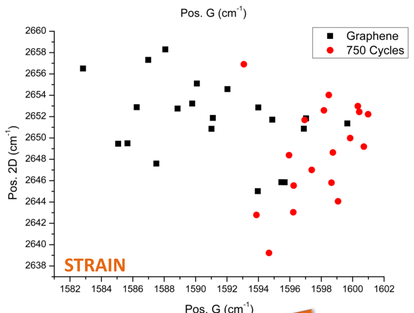


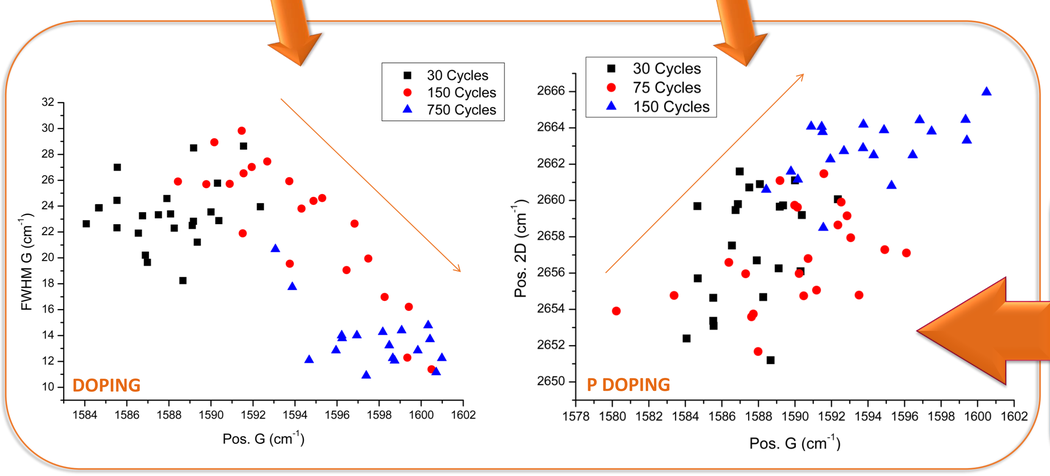








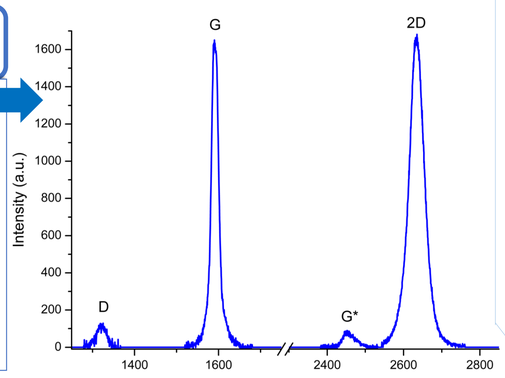




RAMAN SPECTRA

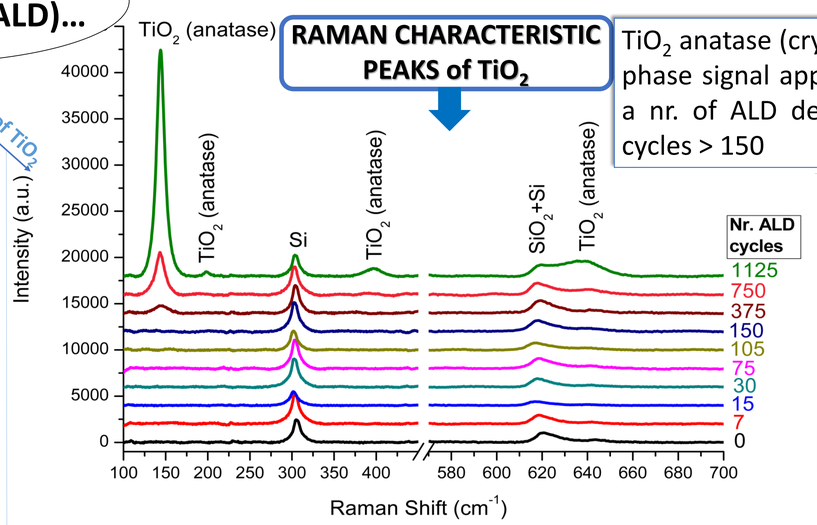
RAMAN CHARACTERISTIC PEAKS of GRAPHENE

- **D**→ defects
- **G**→ in-plane sp^2 C-C stretching phonon modes
- **G***→involves ITO and LA phonons
- **2D**→ in-plane breathing modes

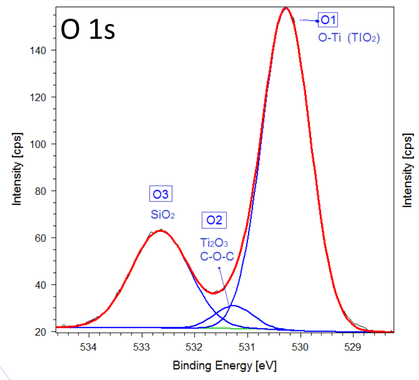


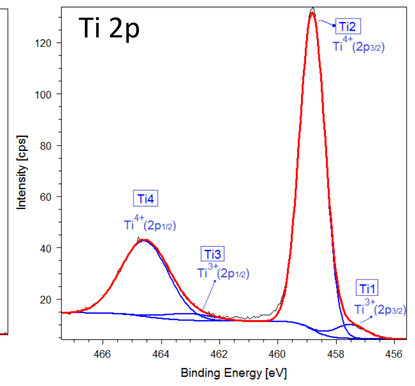
RAMAN CHARACTERISTIC PEAKS of TiO_2

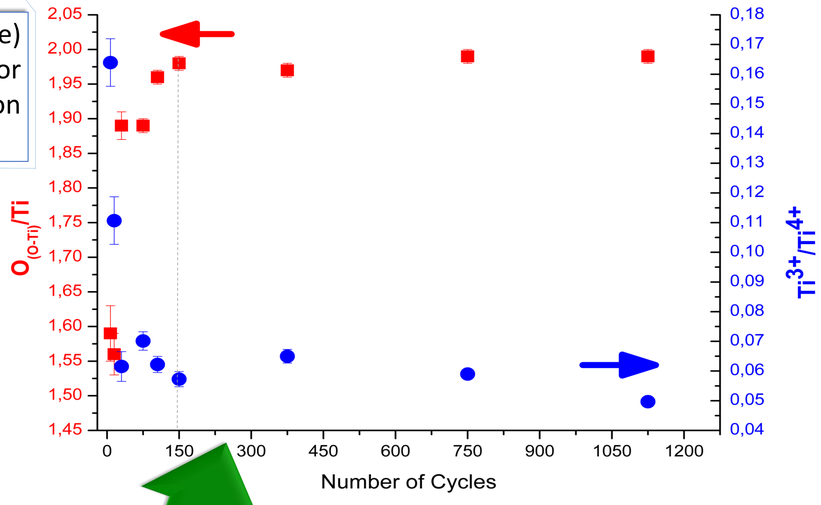
TiO_2 anatase (crystalline) phase signal appears for a nr. of ALD deposition cycles > 150



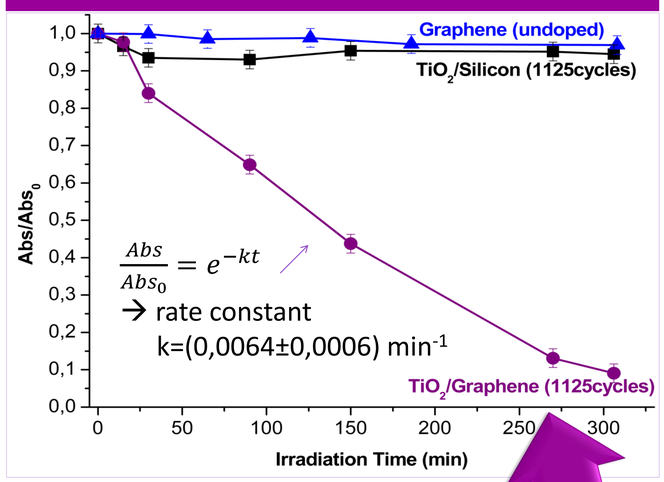
XPS CHARACTERIZATION







PHOTOCATALYTIC ACTIVITY

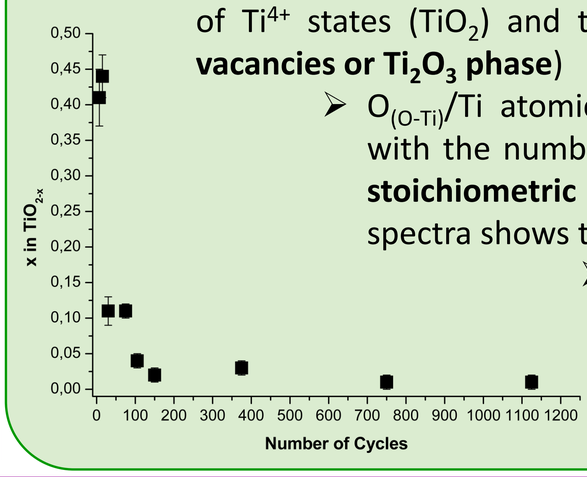


$\frac{Abs}{Abs_0} = e^{-kt}$

→ rate constant

k=(0,0064±0,0006) min^{-1}

- Ti 2p core line should be fitted with the two components of Ti^{4+} states (TiO_2) and the two of Ti^{3+} states (**oxygen vacancies or Ti_2O_3 phase**)
- $O_{(O-Ti)}$/Ti atomic ratio increases exponentially with the number of ALD cycles→ TiO_2 almost **stoichiometric above 150 cycles** (Raman spectra shows the presence of anatase phase)
- The Ti^{3+}/Ti^{4+} ratio have the same trend of the x deviation from ideal TiO_{2-x} stoichiometry → **Ti^{3+} states** are **oxygen vacancies**



- Under UV-Vis irradiation, **TiO_2/Graphene** composite shows the **highest activity**.
- TiO_2/Graphene leads to higher efficiency in **electron-hole separation** (work is in progress to provide a complete understanding of this phenomenon)

- Increasing the number of ALD cycles, in the Raman spectrum of graphene the FWHM G decreases, while the position of the G band increases → **DOPING** occurs
- For all graphene samples decorated with a number of cycles **≤ 150**, both 2D and G peaks positions shift in the same direction → **P DOPING**
- **Above 150** cycles, the variation in the 2D position is higher than that of G band → **STRAIN** (linked to the higher density of anatase phase, which is present)
- Doping is an **INTERFACE** effect (as expected)