Study of the dispersion behavior of aqueous suspensions of titania nanopowder: *hydrothermal sintering application*

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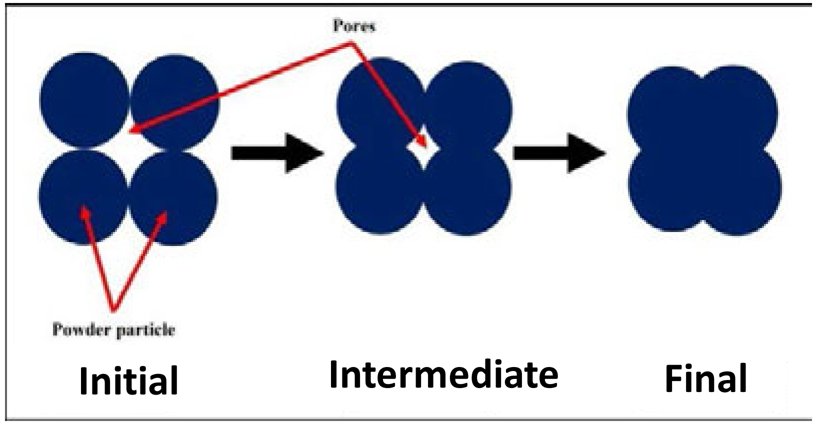
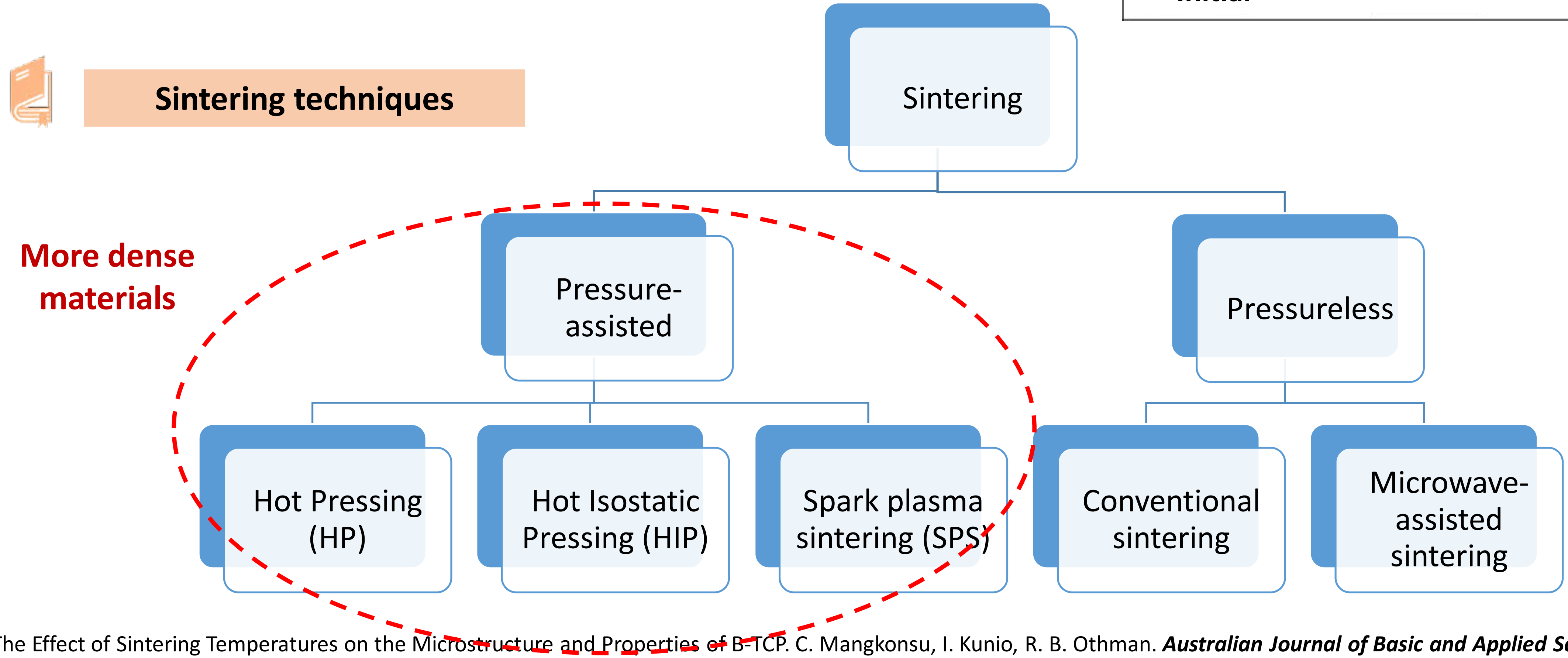
Sintering for ceramics elaboration process



Sintering: heating process of the ceramic green body at very high temperatures (< melting temperature) to eliminate the porosity in the ceramic material and increase its density.

Sintering techniques



The Effect of Sintering Temperatures on the Microstructure and Properties of B-TCP. C. Mangkonsu, I. Kunio, R. B. Othman. ***Australian Journal of Basic and Applied Sciences***, 8(5), **2014**, 492-497.
G. Goglio, A. Ndayishimiye, A. Largeteau, C. Elissalde. View point on hydrothermal sintering: Main features, today's recent advances and tomorrow's promises. ***Scripta Materialia***,158, **2019**,146-152.

- Energy and cost-efficient processes
- Not suitable for metastable materials or that decompose at low temperature
- Increase the particles size and consequently their physico-chemical properties
- Co-sintering of multimaterials is hindered by differences in thermal stability and the physico-chemical compatibilities between the components

How to reduce the sintering temperature

Cold sintering processes: combine pressure and low temperature

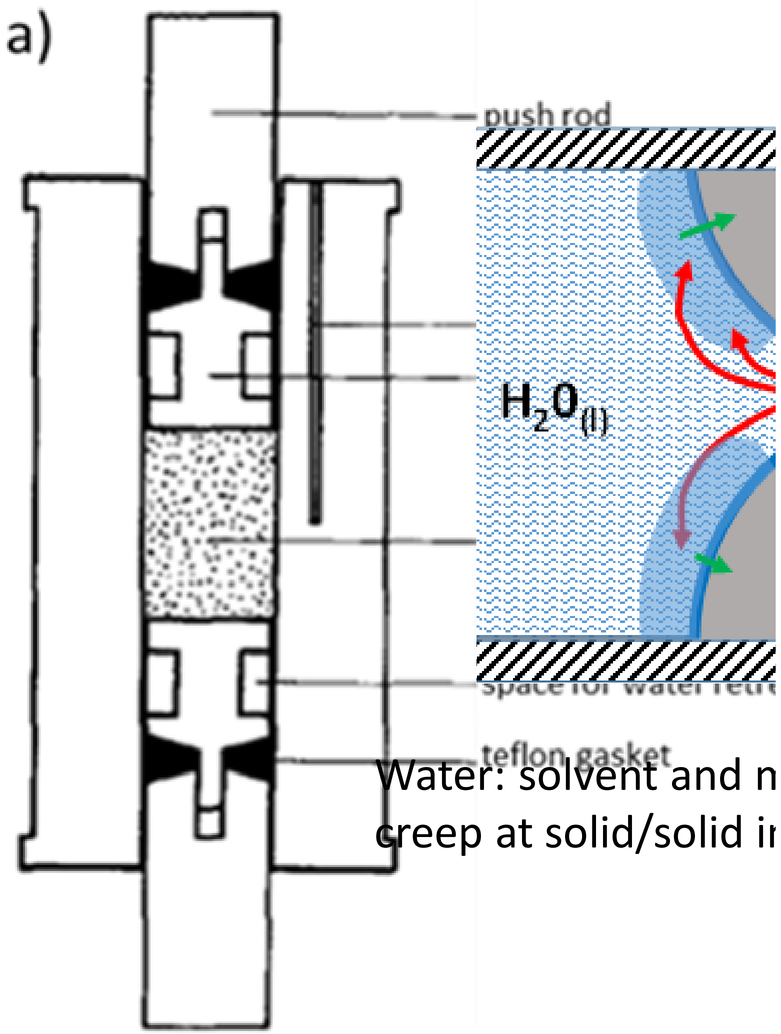
Better control of defects at low temperature

Pressure-assisted sintering

Preserve the physicochemical properties of nanomaterials

Hydrothermal sintering : updated process of the hydrothermal hot pressing method

Developed by *Yamasaki and Yanasigawa* in Japan and improved by Goglio *et al.* in France (Bordeaux)



Water: solvent and m
creep at solid/solid i

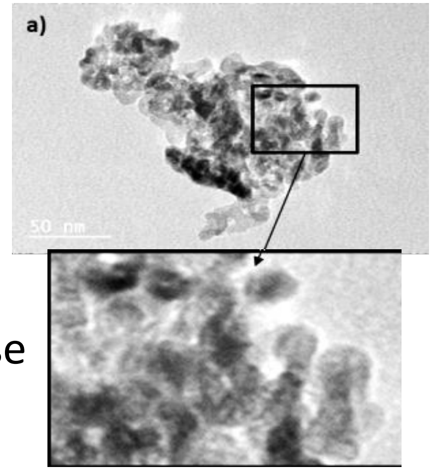
Liquid phase (water)
T <500 °C
Pressure <350 MPa

N.Yamasaki et al. model (Kochi University, Japan) *G. Goglio et al. model* (Université de Bordeaux, France)

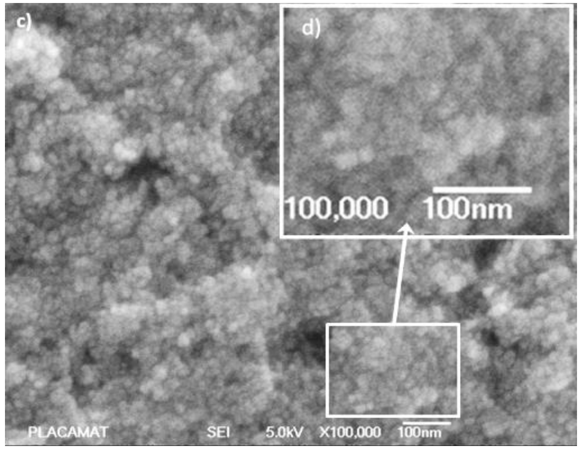
Hydrothermal sintering of TiO_2 nanoparticles !!

Hydrothermal sintering of TiO_2 anatase under **330°C/350 MPa/1h**

TiO_2 anatase
Ø=15 nm



Before sintering



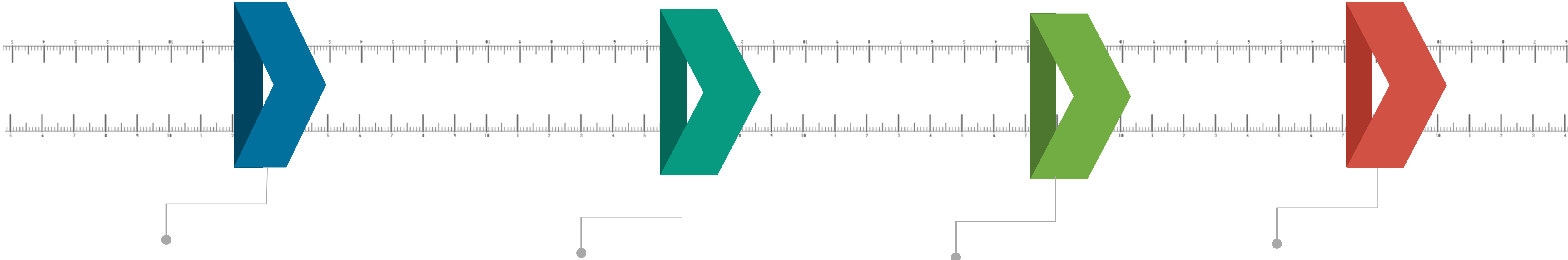
After sintering

Anatase phase

Nanometric size

Only 62% of relative density!!!

Study the pre-sintering steps is fundamental to master the sintering process



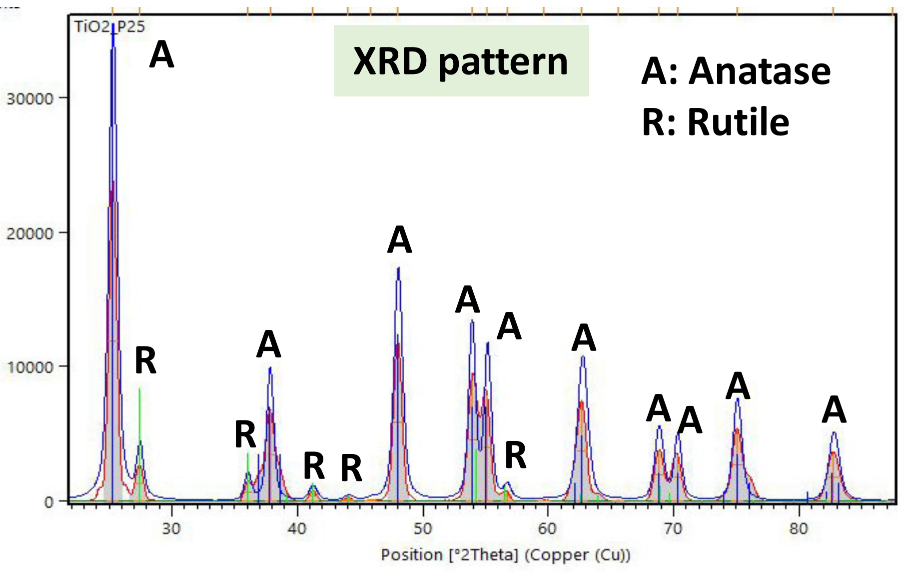
Preparation of dispersed TiO_2 suspensions

Granulation of TiO_2 powders

Optimization of hydration rate in green pellets

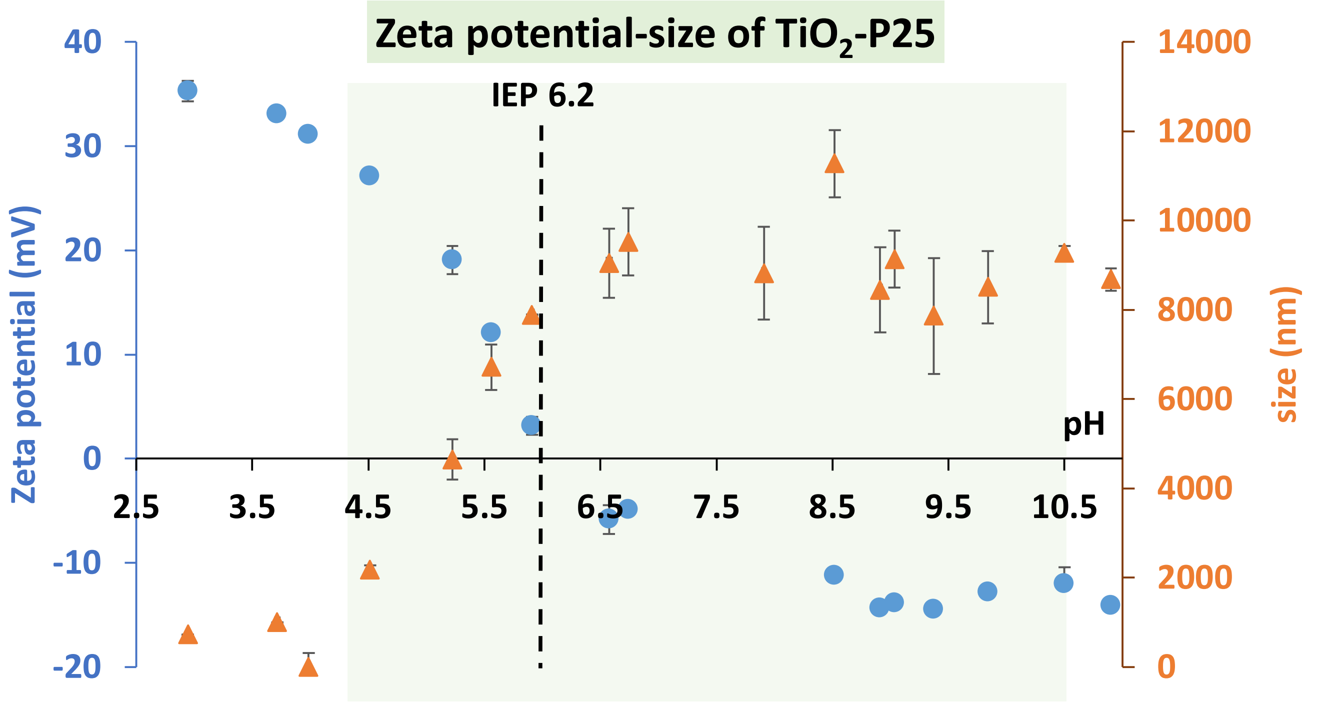
Optimization of the hydrothermal sintering

Characterization of starting material: TiO_2-P25



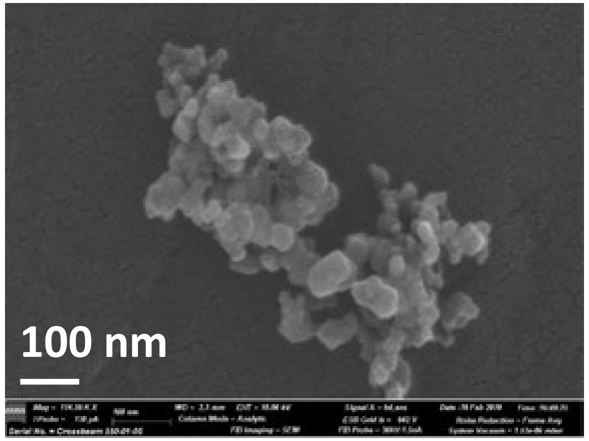
TiO_2_P25: 87 % anatase and 13% rutile

S_{BET}: 59 m²/g, ρ: 3.73 g/cm³



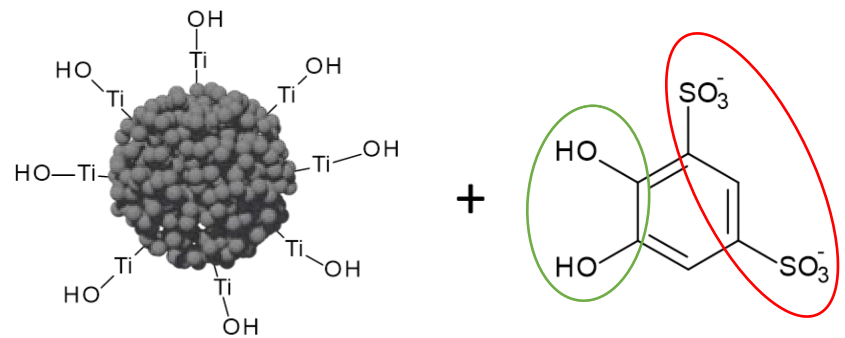
Zetasizer (NaCl 10^{-2} M)

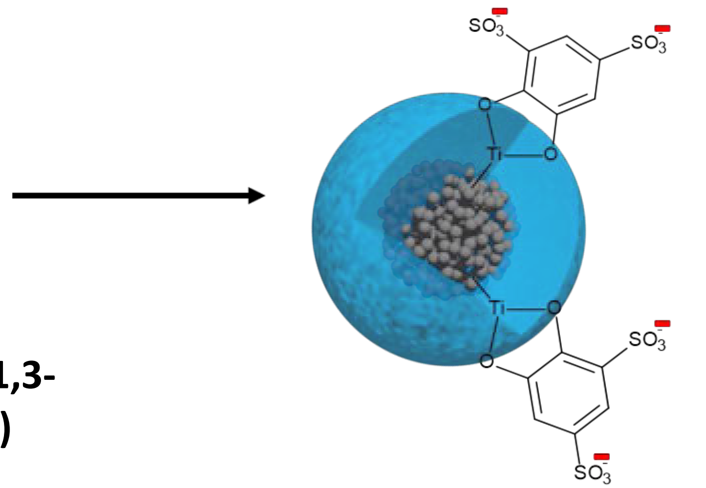
Unstable suspension of TiO_2 in wide range of pH (5-11): agglomeration of nanoparticles



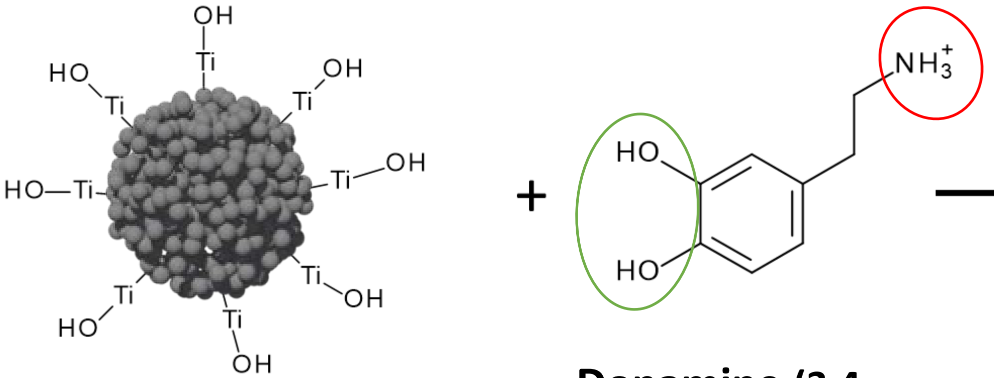
SEM image of TiO_2-P25
20-70 nm

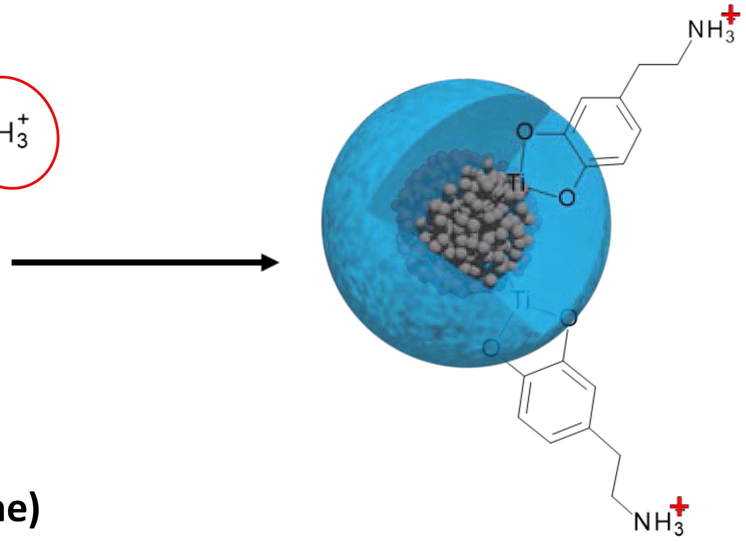
Two dispersants to enhance TiO_2 dispersion





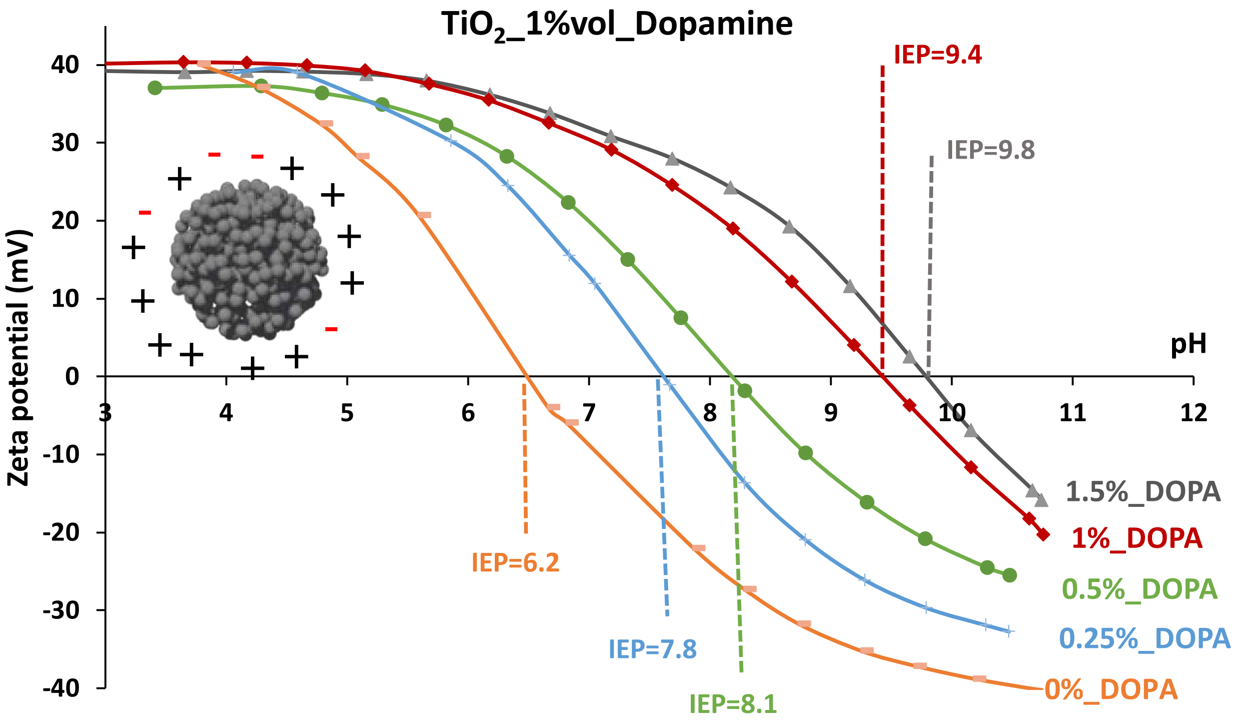
Tiron **(4,5-dihydroxy-1,3-benzenedisulfonate)**



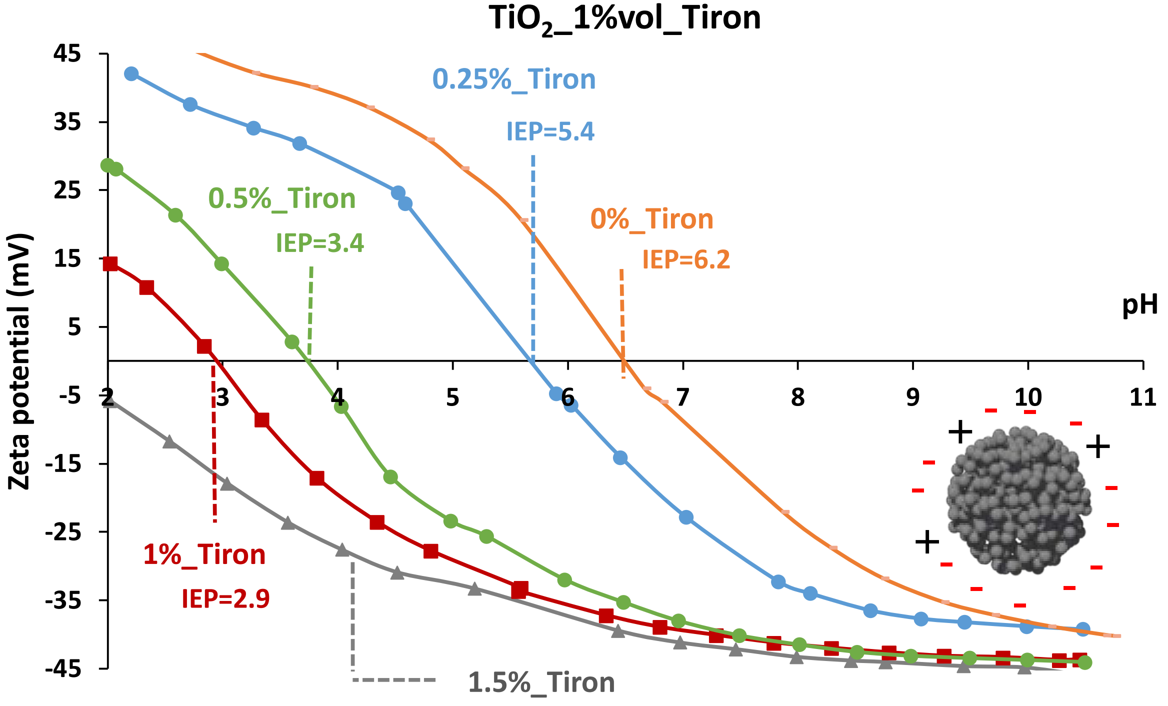


Dopamine **(3,4-dihydroxyphenethylamine)**

Elaboration of dispersed suspensions of TiO_2 nanoparticles: effect on the surface charge



Dispersants (Tiron and Dopamine) increase the pH range of stability

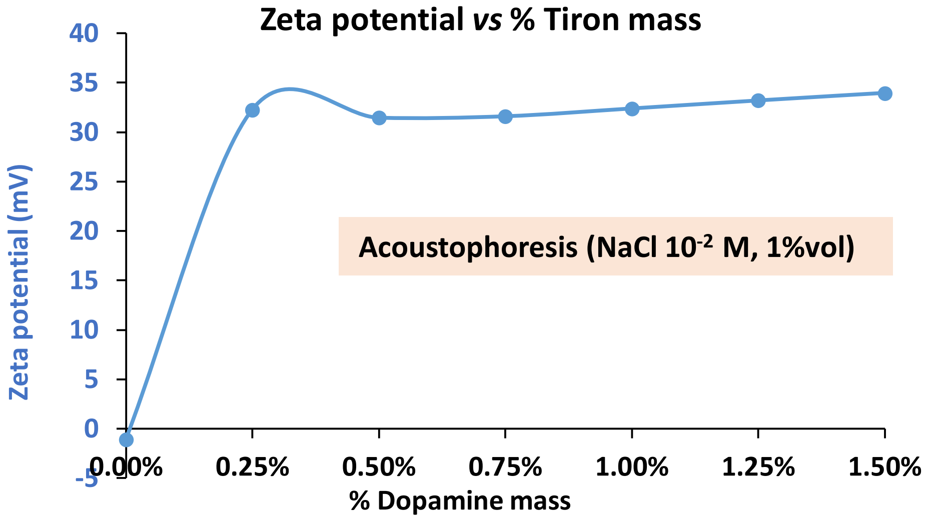


Tiron inverses the global charge of TiO_2 nanoparticles (NPs) and dopamine keeps the positive charge

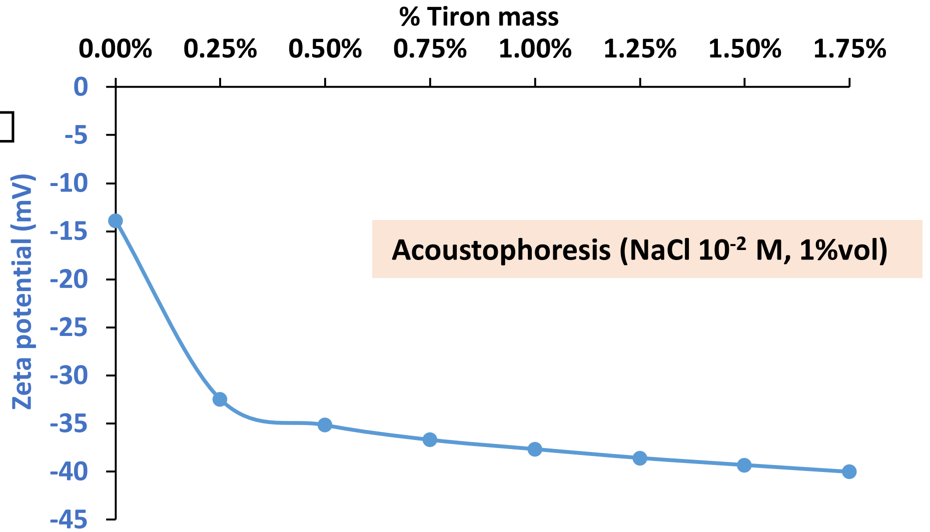
Tiron decreases the isoelectric point (IEP) and dopamine increases it to 9.8

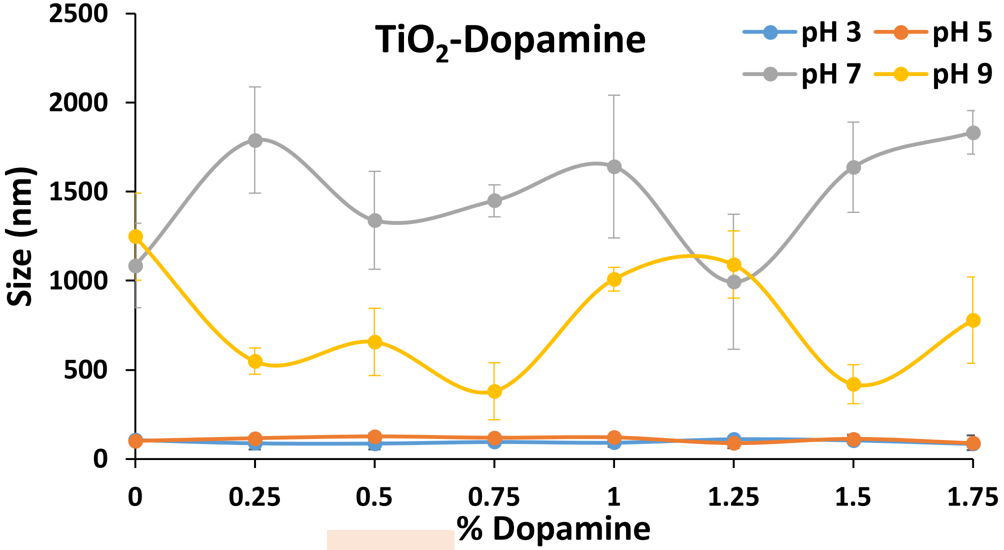
Acoustophoresis (NaCl 10^{-2} M)

Elaboration of stable suspensions of TiO_2 nanoparticles: dispersant and pH effect



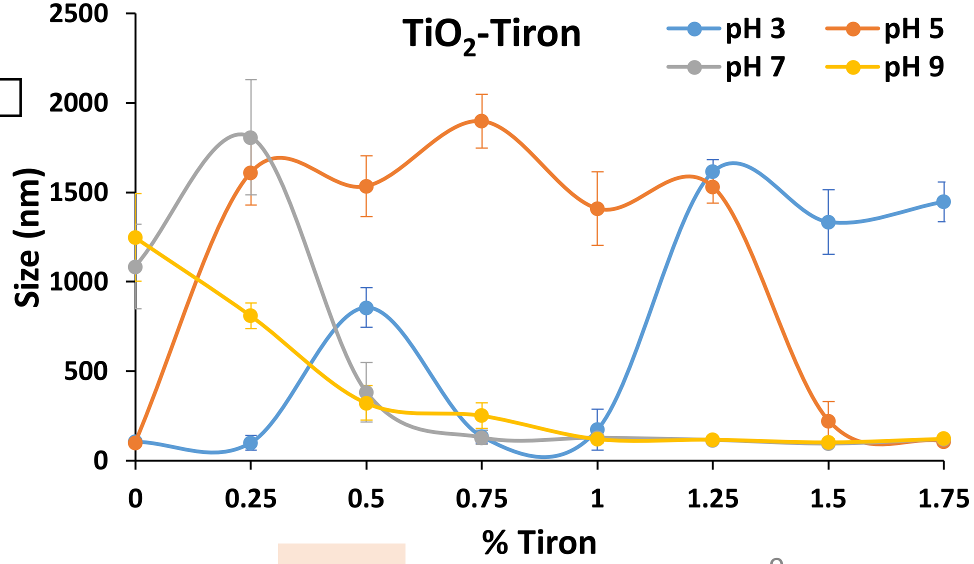
Dispersant enhances nanoparticled (NPs) stability by increasing zeta potential values





DLS

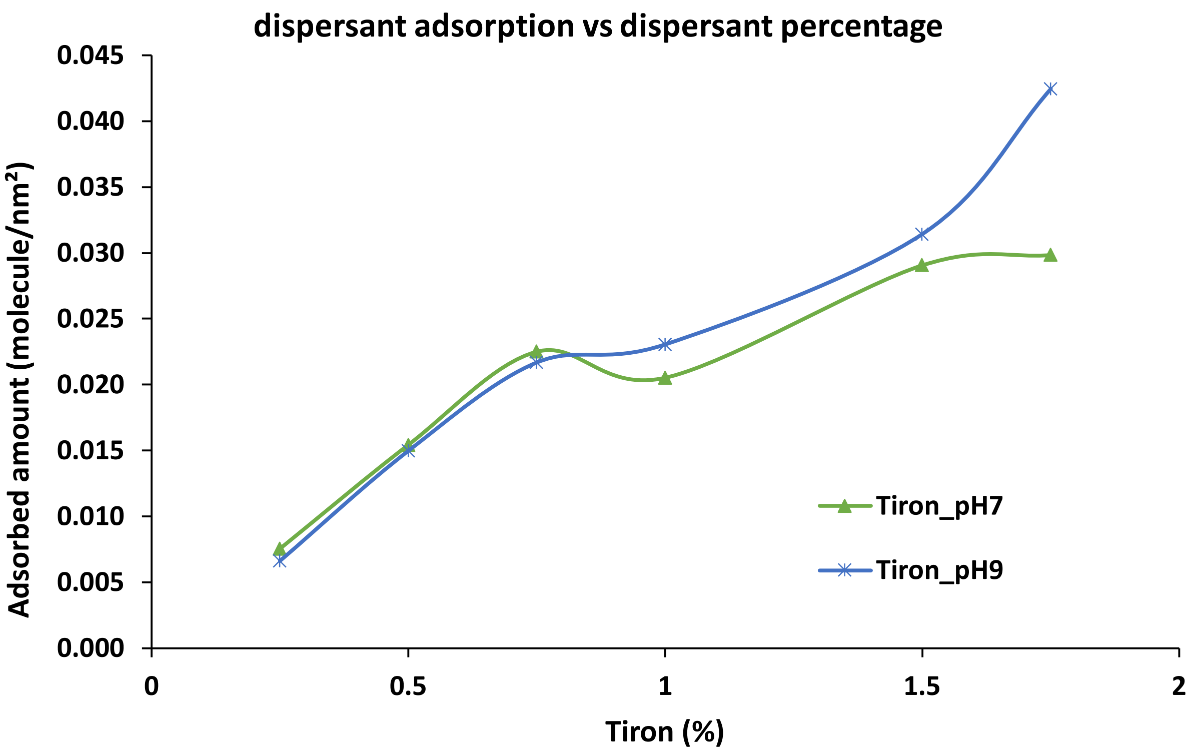
Tiron stabilizes NPs at basic medium and Dopamine stabilizes NPs at acid medium



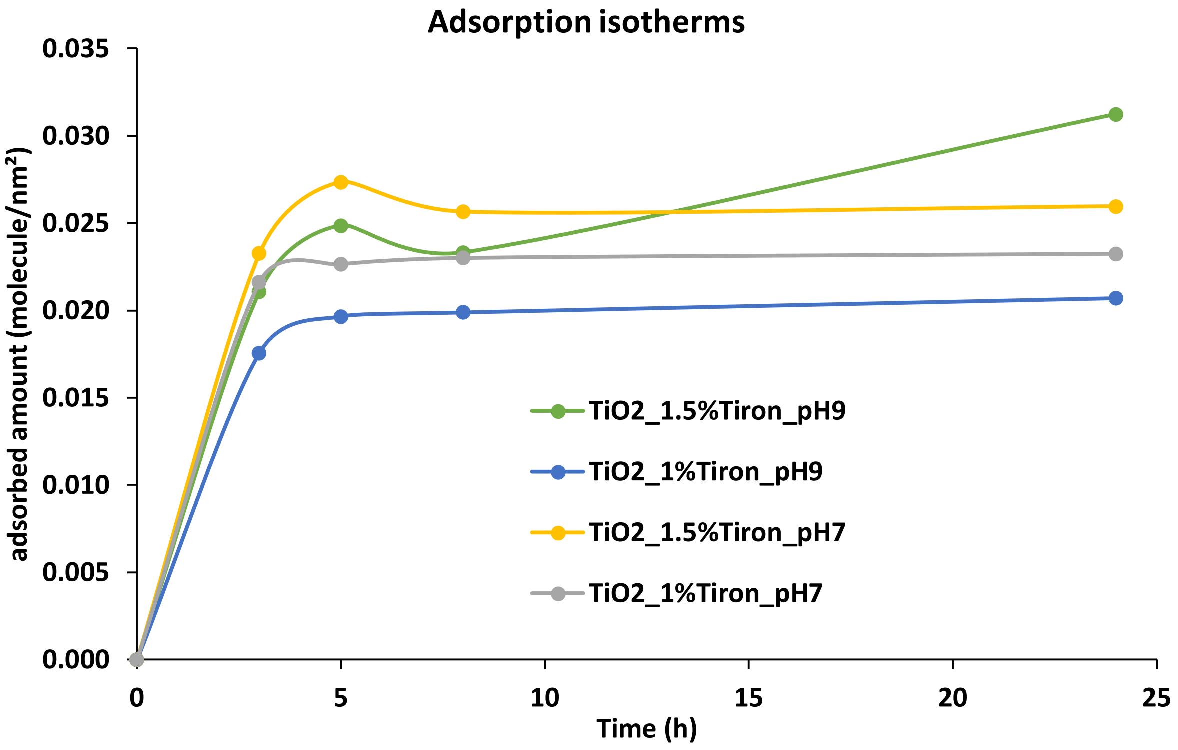
DLS

pH and dispersant concentration govern the NPs stability

Study of the Tiron adsorption onto TiO_2 surface



UV-Visible (TiO_2, 2%vol, 24h)

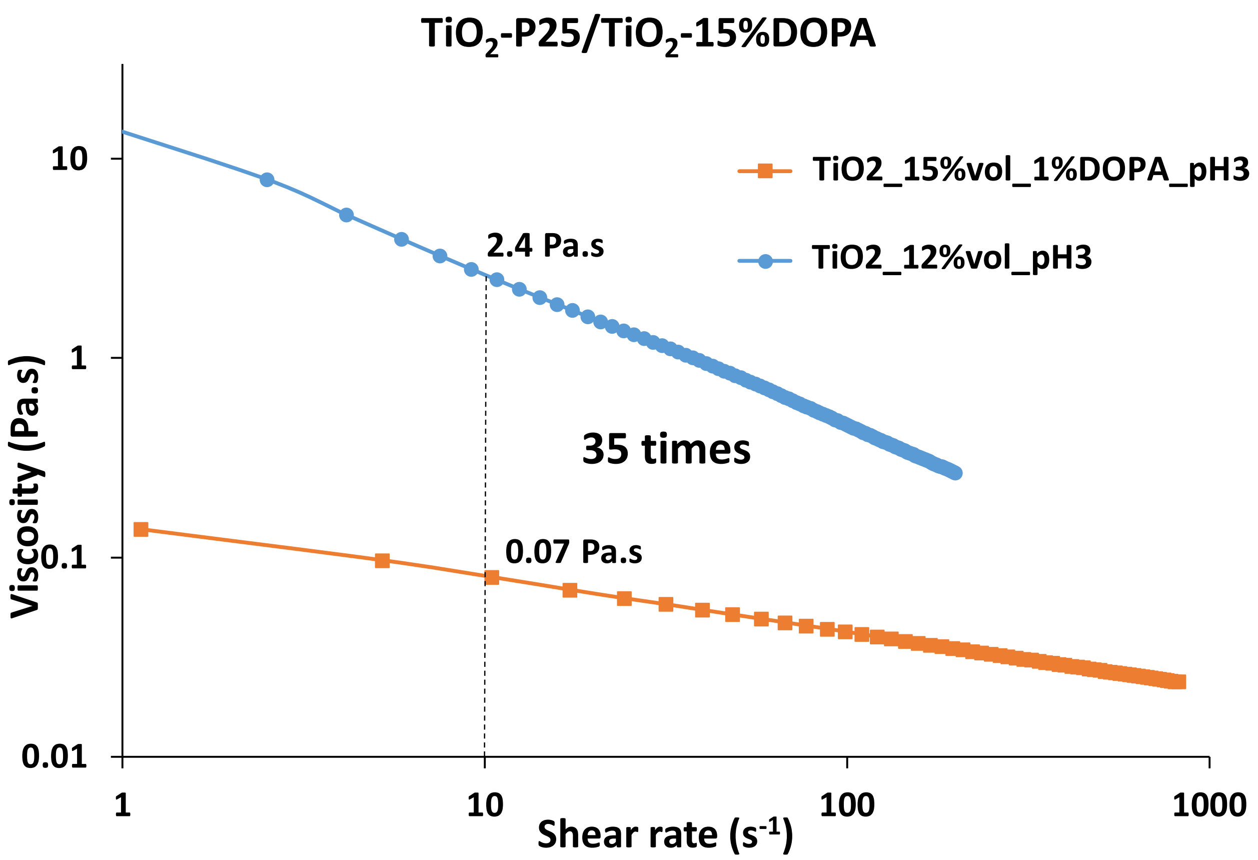


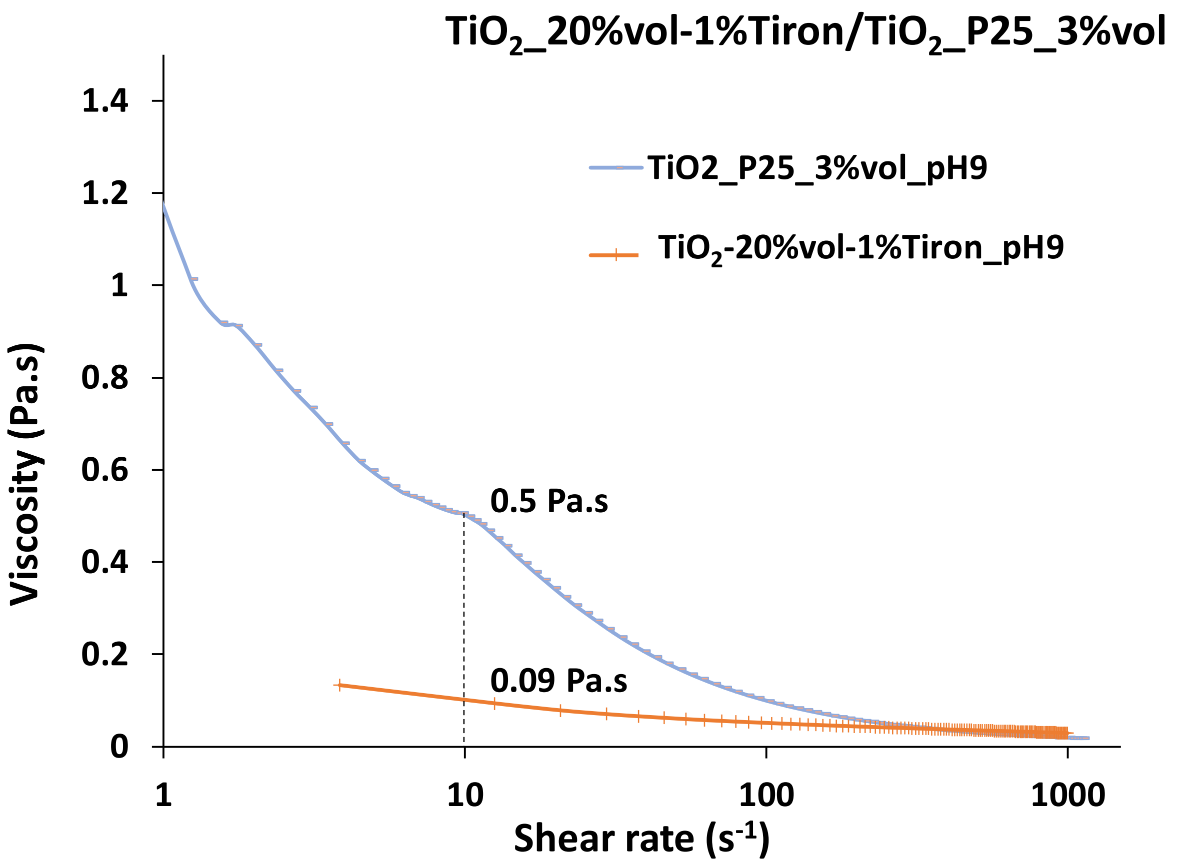
UV-Visible (TiO_2, 2%vol)

The most adsorbed amount of Tiron is obtained at pH9

At pH 7, fast adsorption of Tiron: covalent and electrostatic interactions between NPs and Tiron

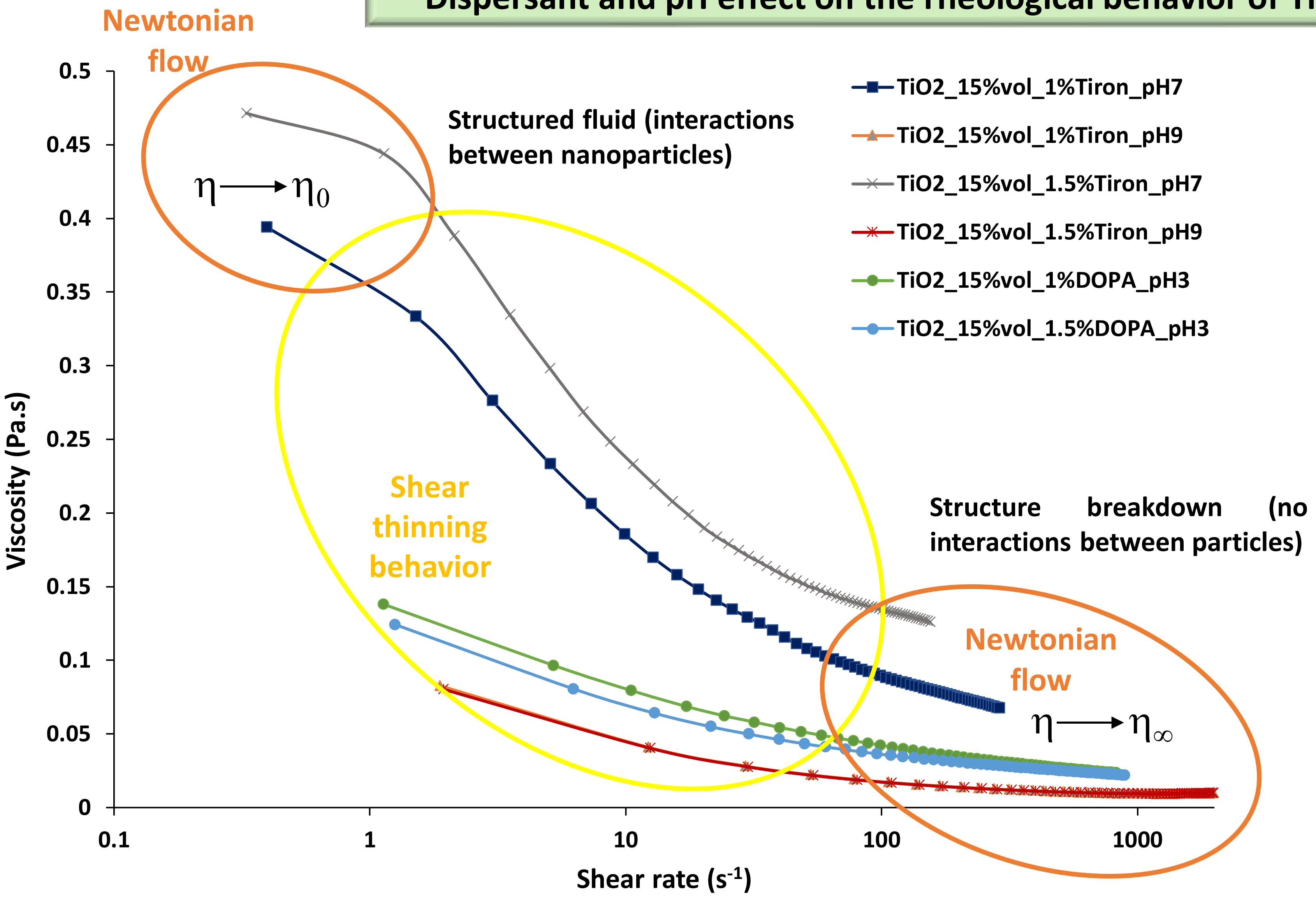
Dispersant effect in the flow behavior of concentrated suspensions based on TiO_2





The use of dispersant is essential to prepare concentrated suspensions of TiO_2

Dispersant and pH effect on the rheological behavior of TiO_2 suspensions

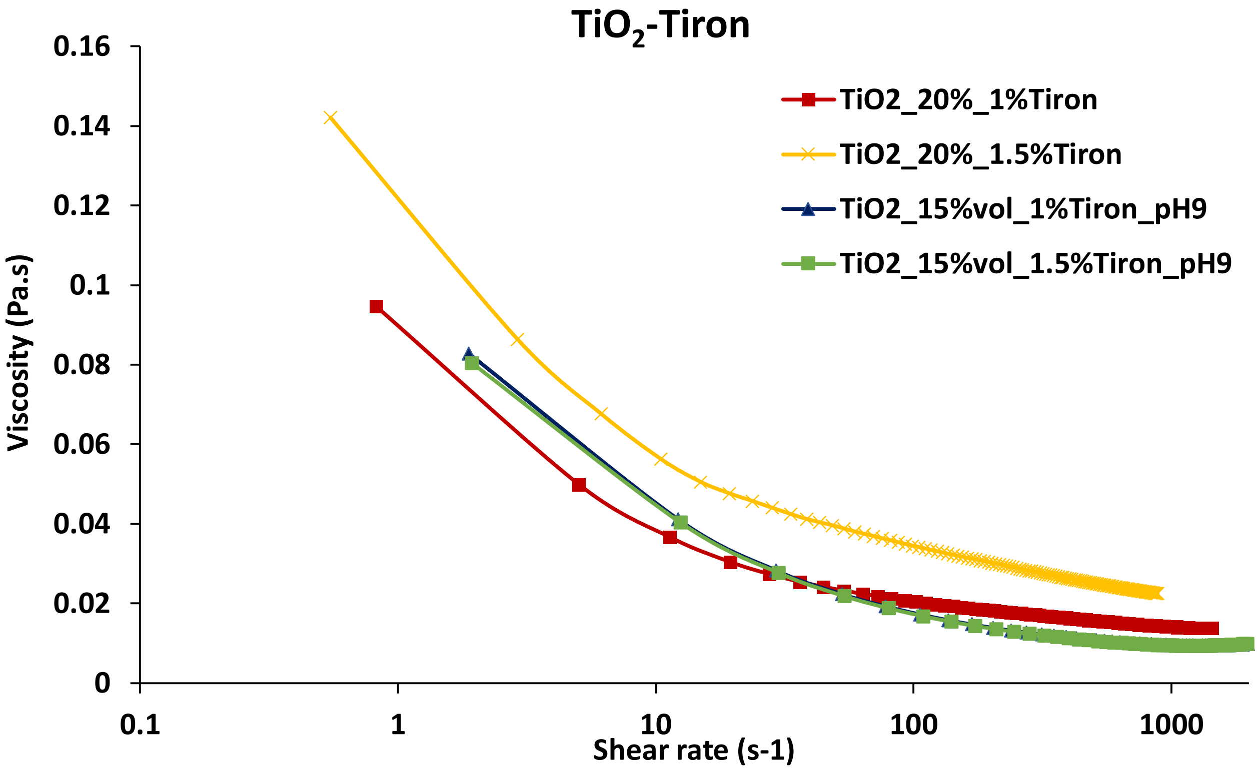


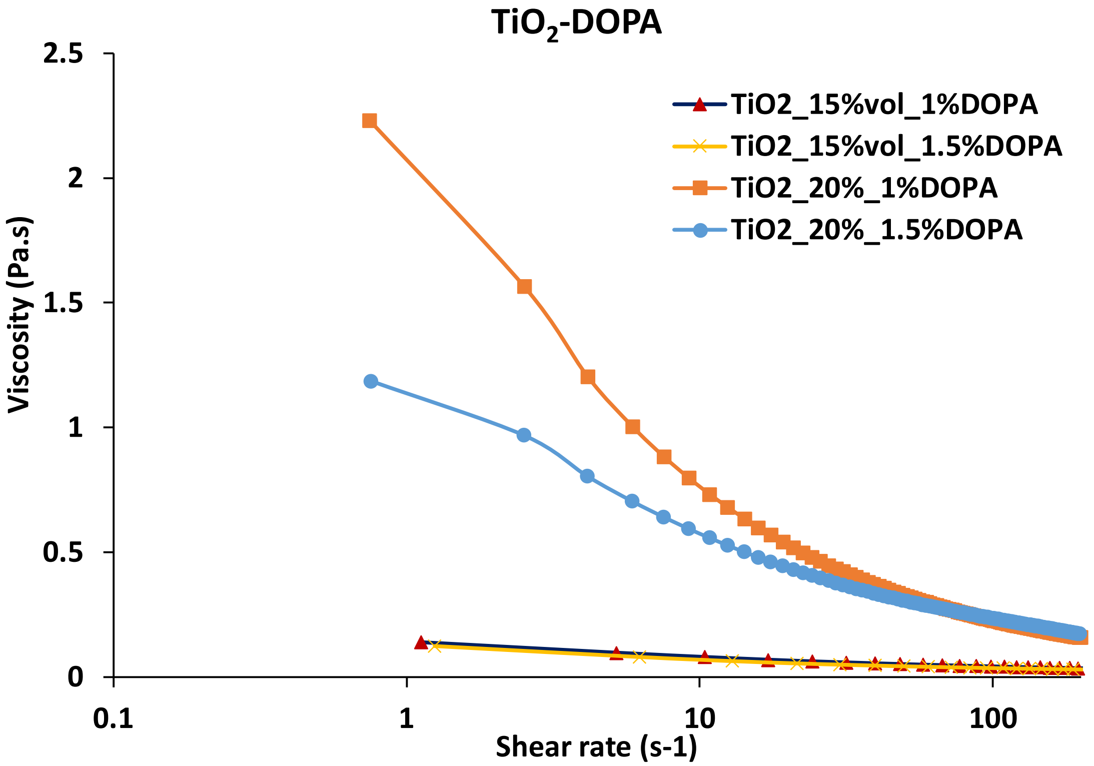
Plastic flow at pH7 and pseudoplastic behaviour at pH9

pH influences the rheological behavior and its effect is accentuated at high concentrated suspensions even for the same nanoparticles size and surface charge.

Tiron-modified titania suspensions at pH 9 are more fluid than dopamine-modified titania suspensions at pH3

Rheological behavior of TiO_2 suspensions at different solid content

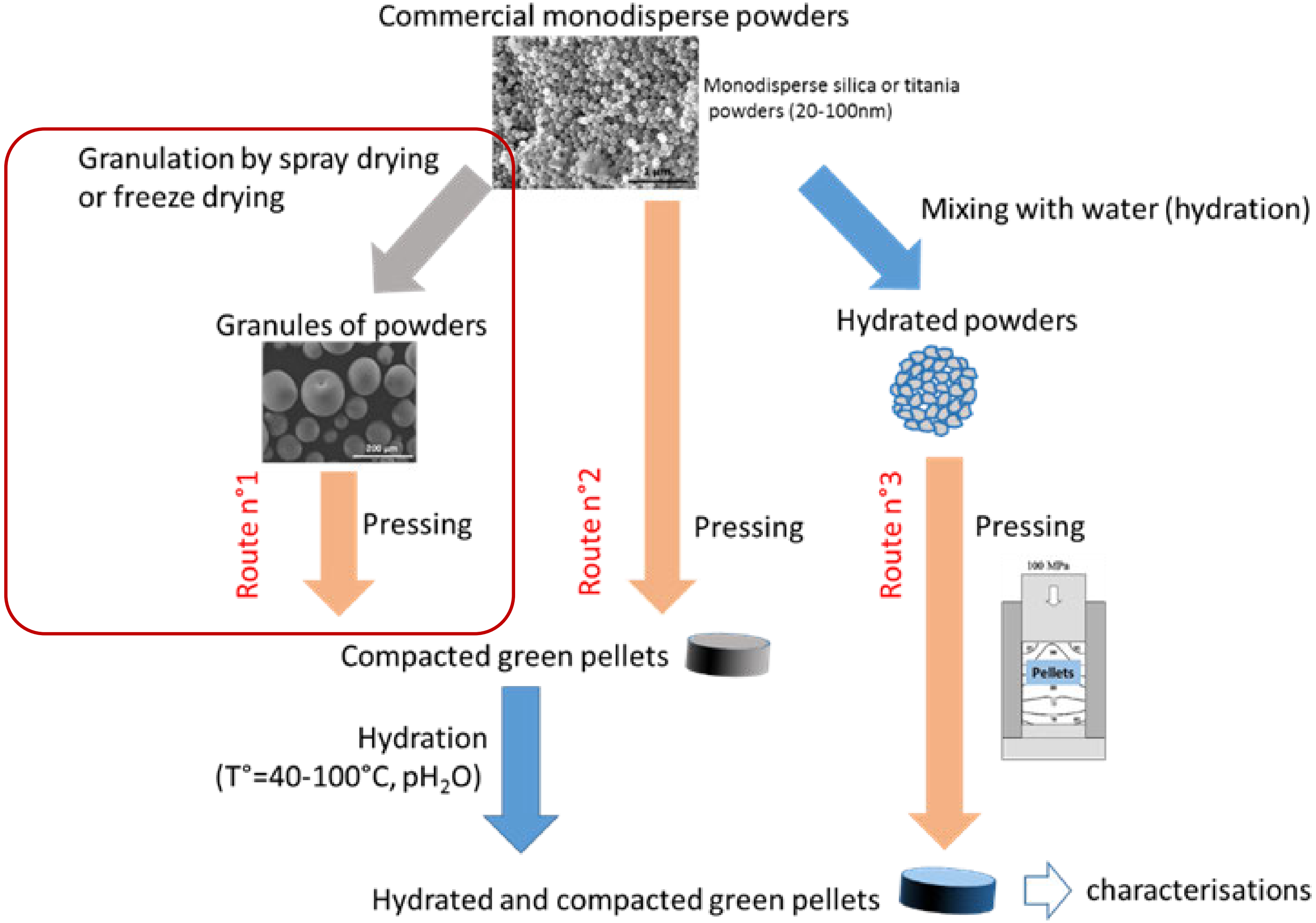




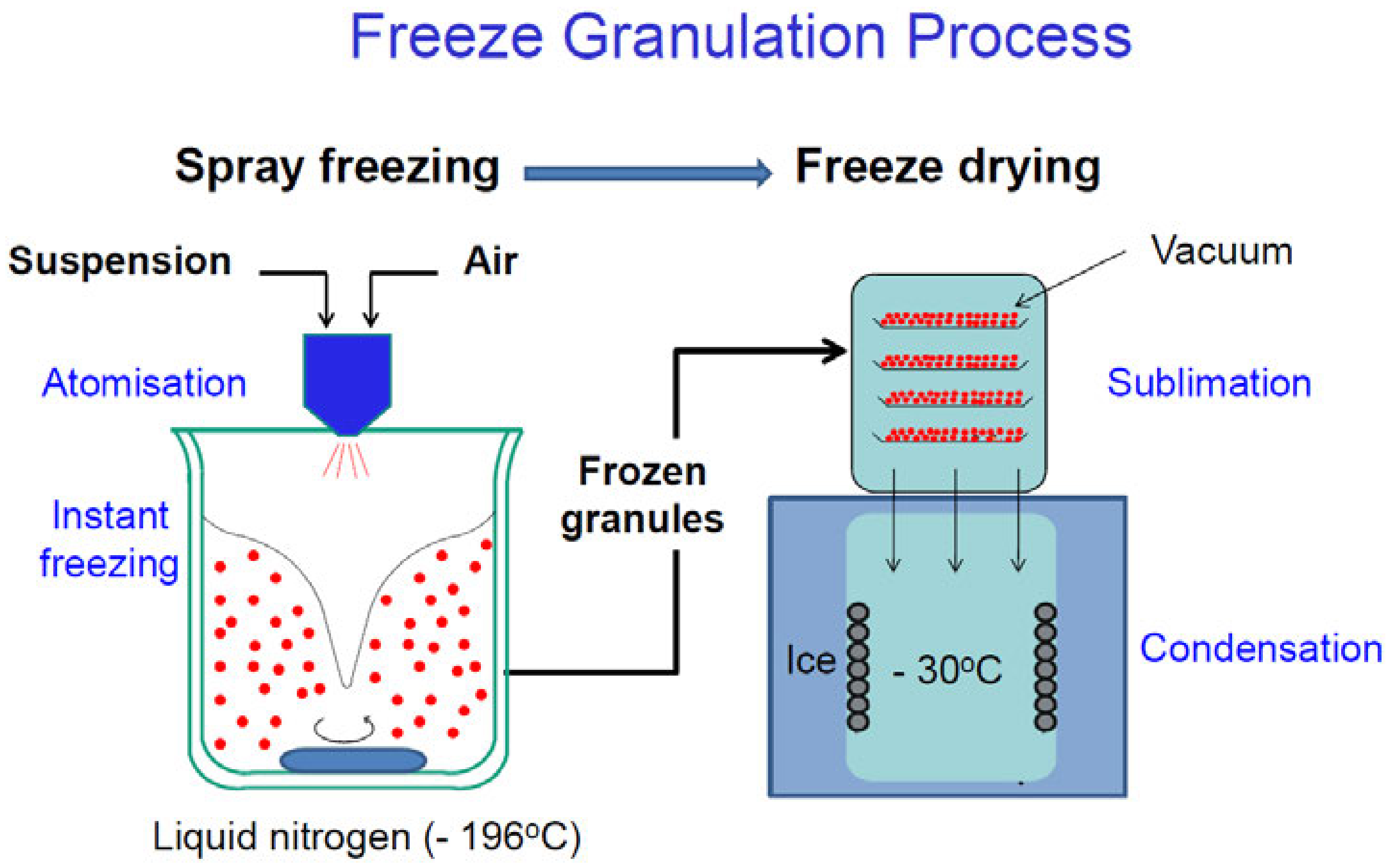
From 15%vol to 20%vol TiO_2, suspensions become more viscous for Dopamine but not a big difference is noted for TiO_2-Tirons suspensions

15%vol of TiO_2 is retained for DOPA-TiO_2 suspensions however 20%vol was chosen for Tiron-TiO_2 suspensions

Characterization of granulated powder



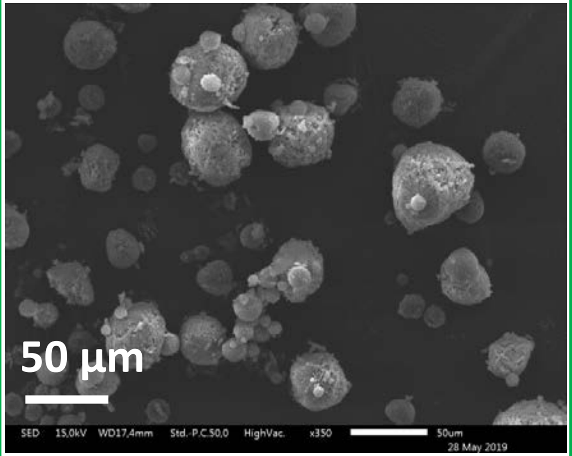
Freeze granulation: for which reason?



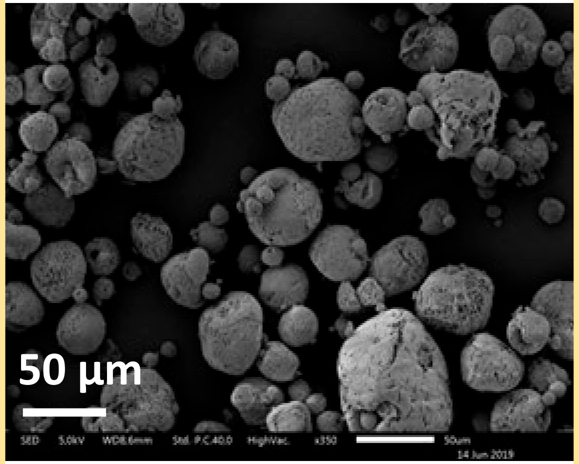
The granulation is usually required for the pressing of ceramic powders to obtain an homogenous and high compactness in green pellets.

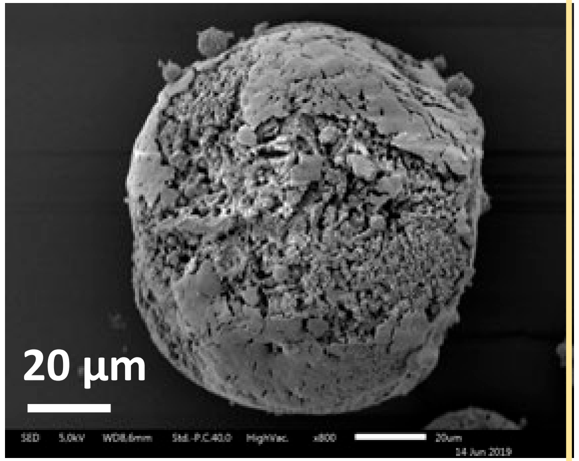
Improves the powder flowability and prevents individual particles from becoming airborne.

Morphology of the granulated powders: SEM images



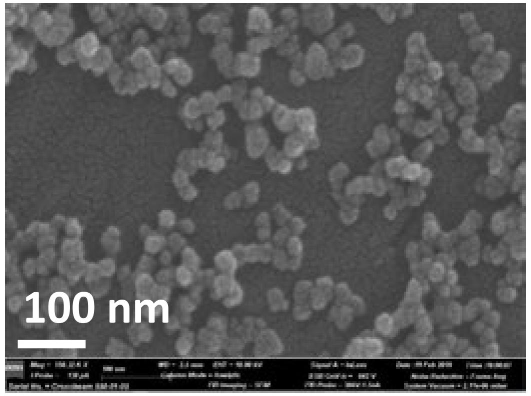
15%vol_1.5%DOPA





20%vol_1.5%Tiron

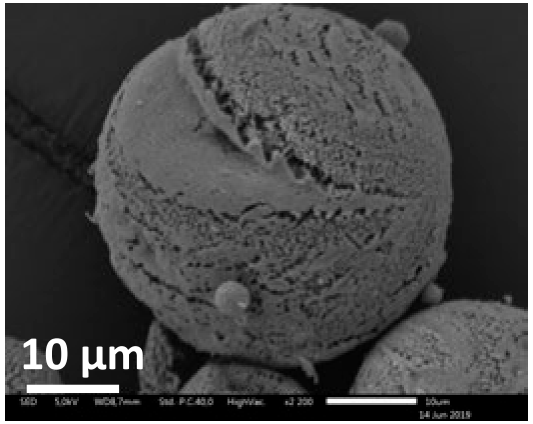
Micrometric size and spherical-shaped granules



- Bare TiO_2
- Nanometric size

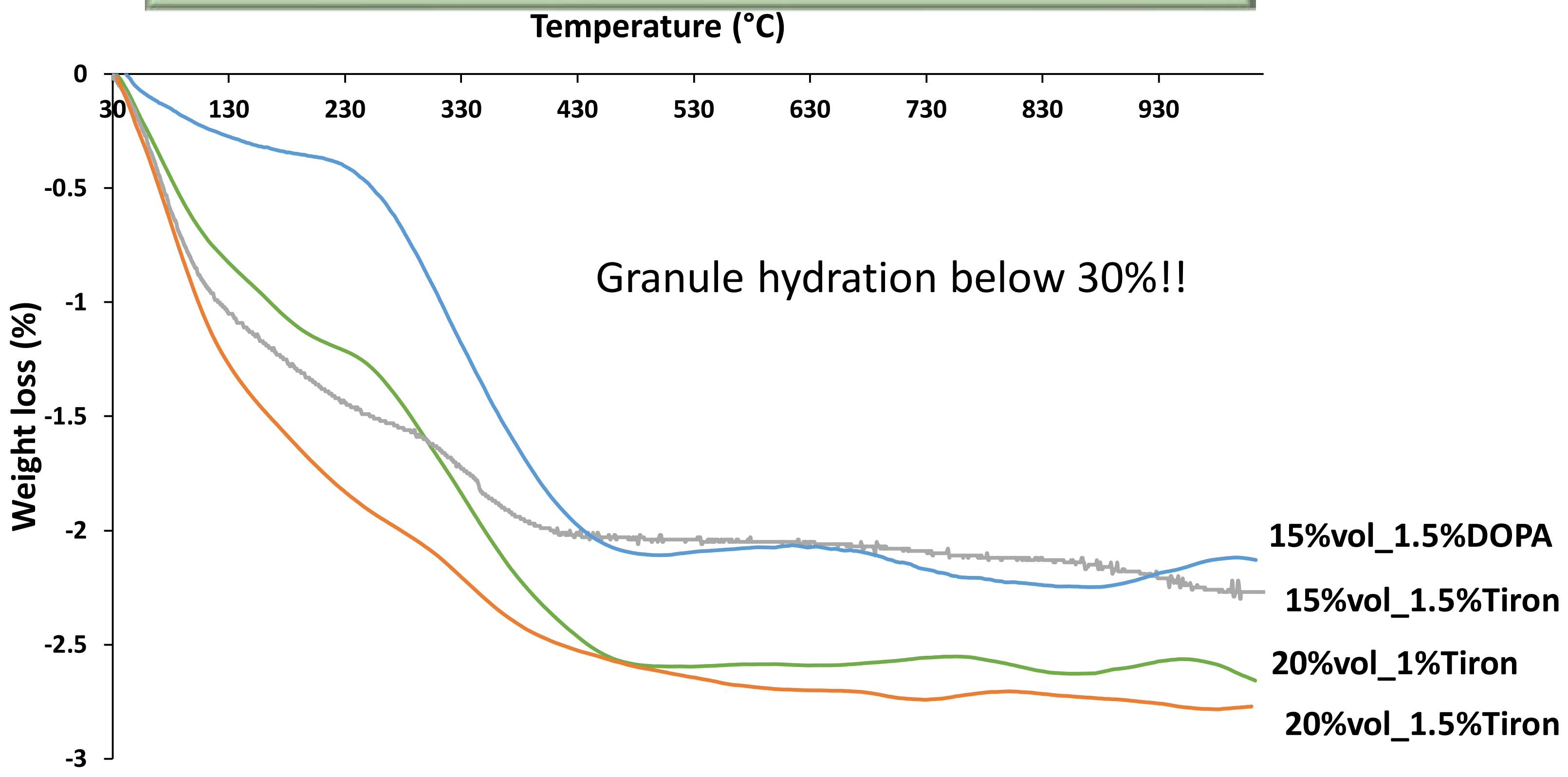
Concentrated Suspension

Granulation



- Modified-surface granule
- Micrometric size
- Ready for formulation into pellets

Thermogravimetric analysis of granulated powders



Outlooks:

Optimize the hydration rate and water distribution in the green pellets by controlling the freeze-drying time

Optimize the size distribution of the granulated powders

Optimize the hydrothermal sintering conditions for TiO_2 and other types of materials

Thank you for your attention

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