

Direct synthesis of $\text{RuO}_2/\text{TiO}_2$ nanoparticles with core/shell structure for potential catalytic application

Task: Aerosol droplet size

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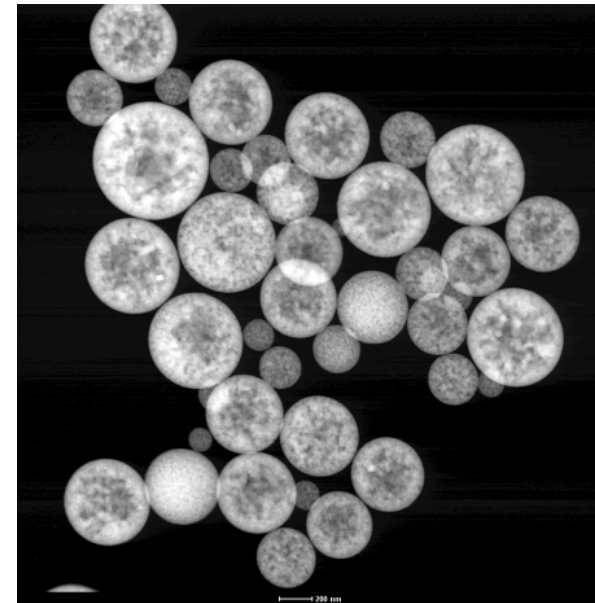
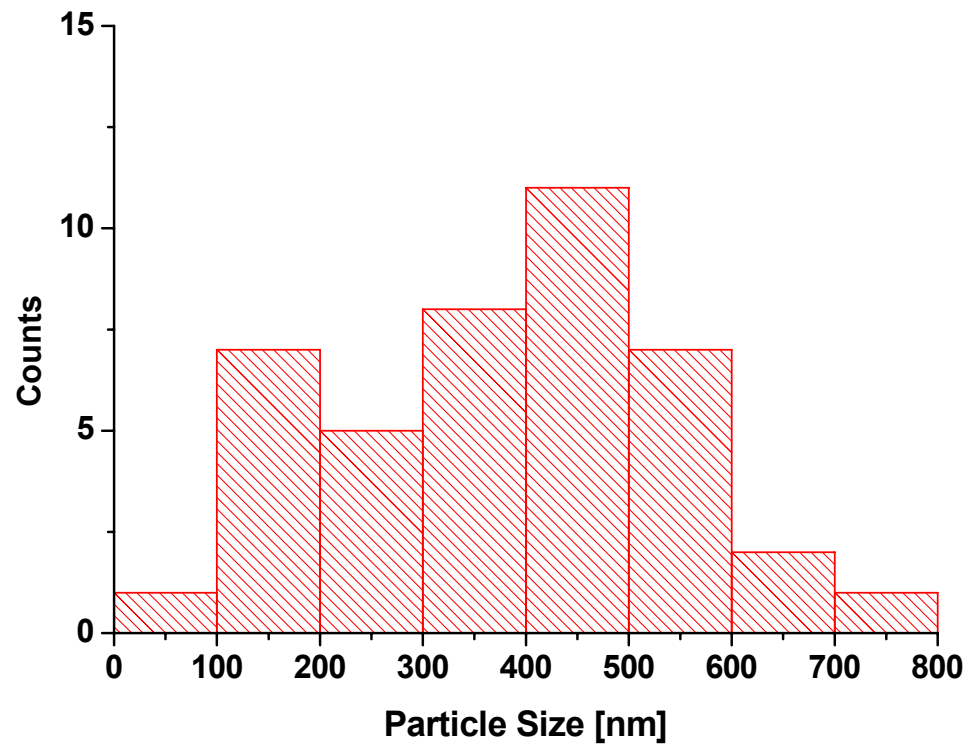
IME Metallurgische Prozesstechnik und Metallrecycling
RWTH Aachen

Prof. Dr.-Ing. Bernd Friedrich

Previous results: Calculated and measured particle size

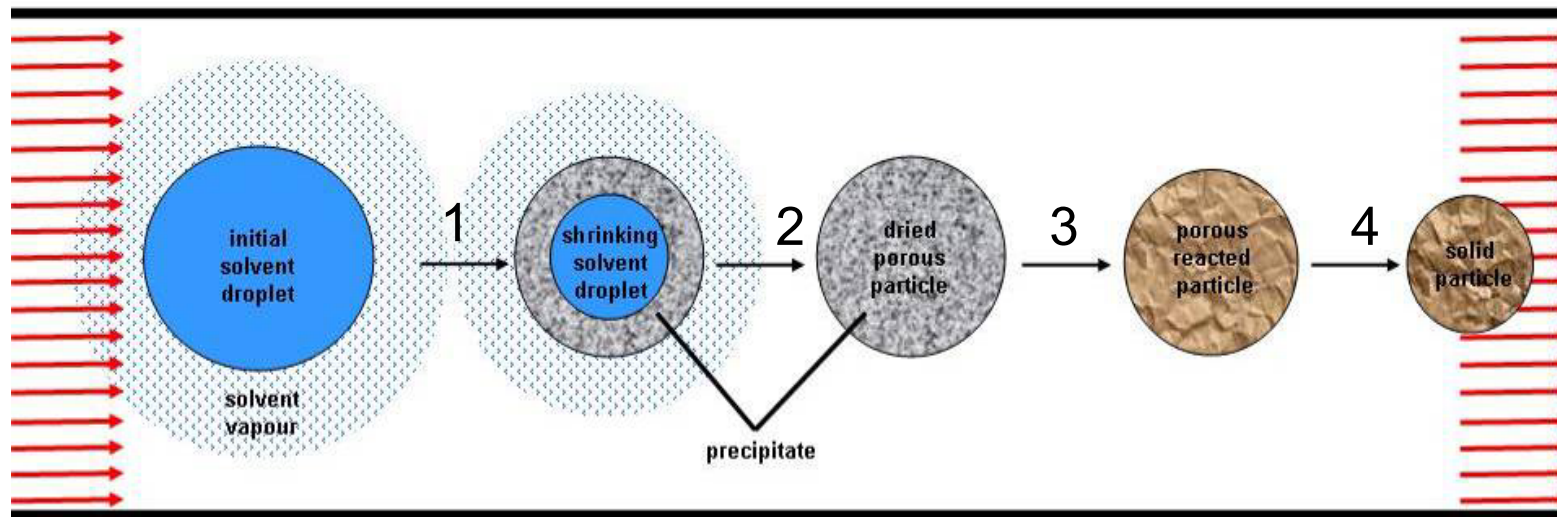
$$D_p = D_t \left(\frac{c_{\text{RuCl}_3} \cdot M_{\text{RuO}_2}}{\rho_{\text{RuO}_2} \cdot M_{\text{RuCl}_3}} \right)^{\frac{1}{3}}$$

D_p	Diameter of particle size of ruthenium oxide (μm)
D_t	Diameter of aerosol droplet for water solution (μm)
c_{RuCl_3}	concentration of the aq. solution of RuCl_3 (mol/cm^3)
M_{RuCl_3}	Molar mass of ruthenium chloride (g/mol)
M_{RuO_2}	Molar mass of Co (g/mol)
ρ_{RuO_2}	Density of o (g/cm^3)



parameter:
 $\text{RuO}_2/\text{TiO}_2:0.33$
 atmosphere: O_2
 precursor: $\text{RuCl}_3 \times 3\text{H}_2\text{O}$; $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$; HCl ; H_2O

synthesis of nanoparticle from aerosol droplet



1. Evaporation 2. Precipitation 3. Chemical reaction 4. Sintering

$$D_{\text{droplet}} = 0.34 \cdot \left(\frac{8\pi \cdot \gamma}{\rho \cdot f^2} \right)^{\frac{1}{3}}$$

D diameter of aerosol droplet [μm]
 γ surface tension of liquid [N/m]
 ρ density of liquid [g/cm^3]
f frequency of ultrasound [$1/\text{s}$]

Influence:

- concentration \rightarrow density & surface tension of solution
- frequency

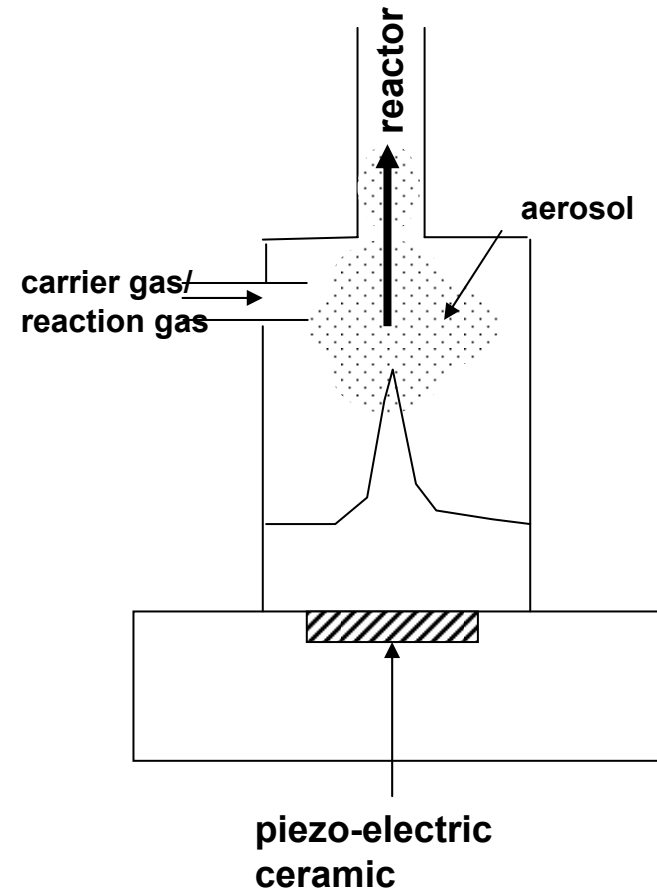
Main Aims

Measurement of droplet diameter to :

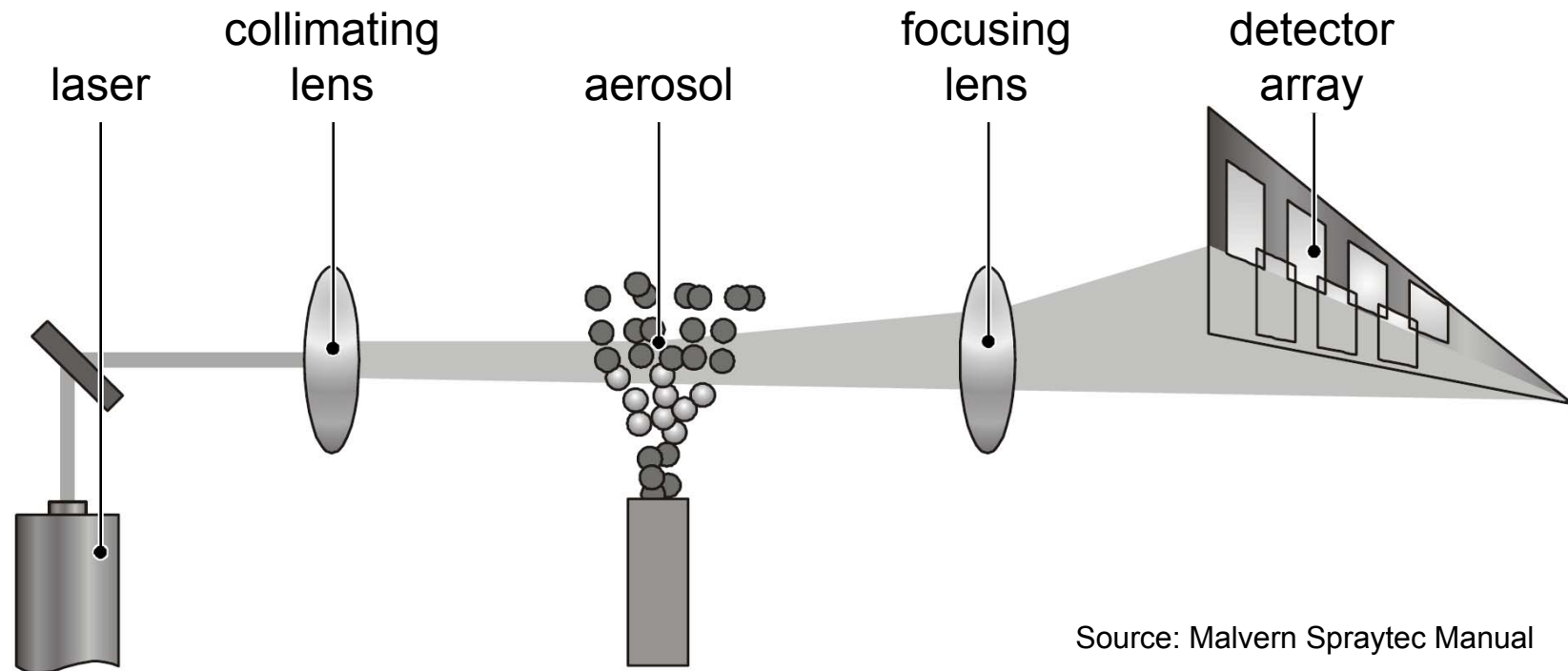
- find out droplet size distribution
- compare measurement with calculation

- Building of new experimental setup for the proposed measurement (KIT)
- Measurement of droplet size for an ultrasonic generator (0.8 and 2.5 MHz)
- Calculation of theoretical values for droplets
- Comparison of theoretical and experimental droplet values

Aerosol production by ultrasonic sound:



Droplet size distribution (Spraytec, Malvern)



Source: Malvern Spraytec Manual

Laser light is scattered by the aerosol droplets. Scattering angle depends on droplet size.

Scattering signal is recorded by detector array and processed by software to correlating droplet size distribution.

Experimental procedure for droplet size measurement

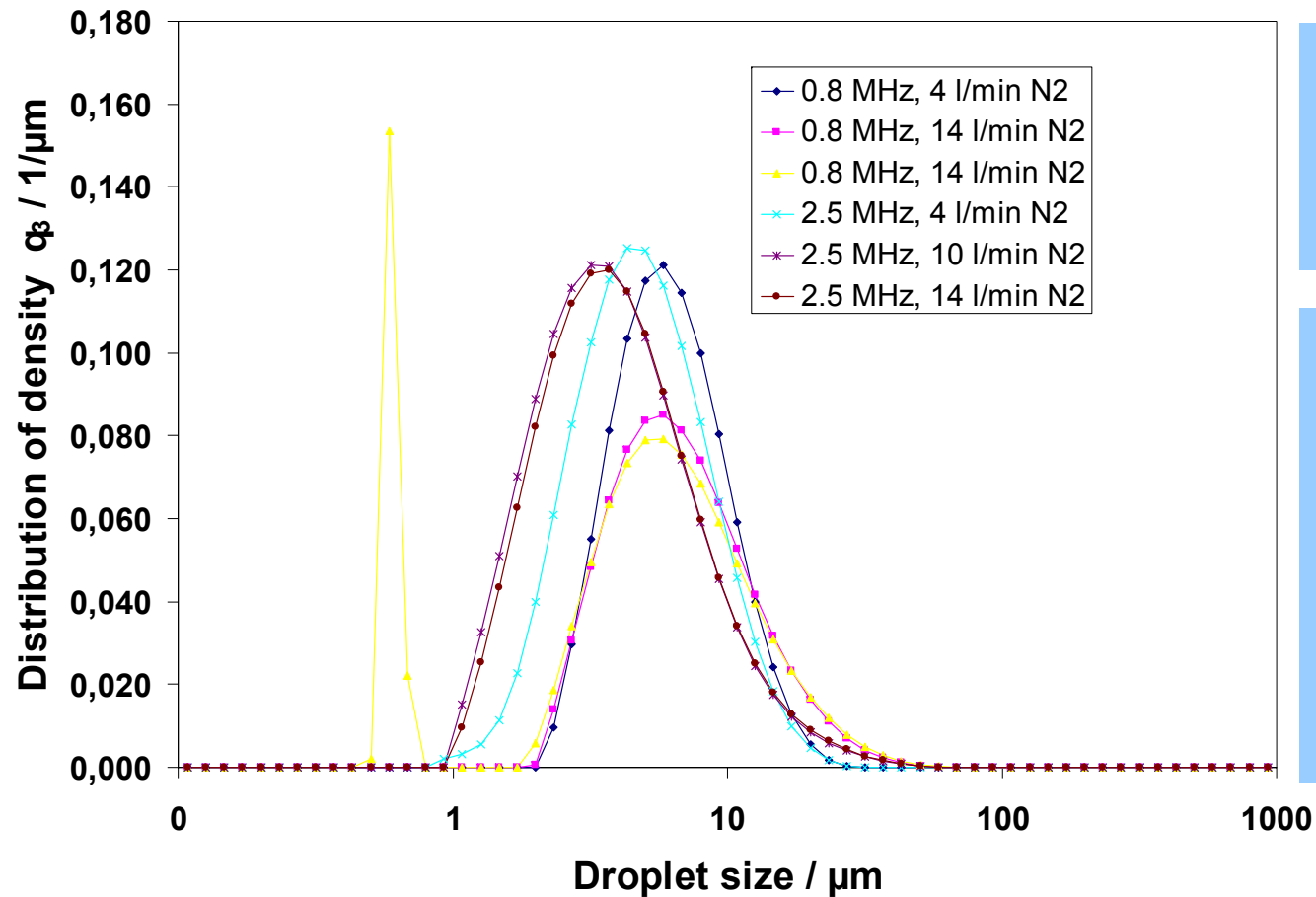


Measurements of the droplet size at the KIT
(Karlsruhe Institute of Technology)



USP production of aerosol with
3 ultrasonic transducer
(IME RWTH Aachen)

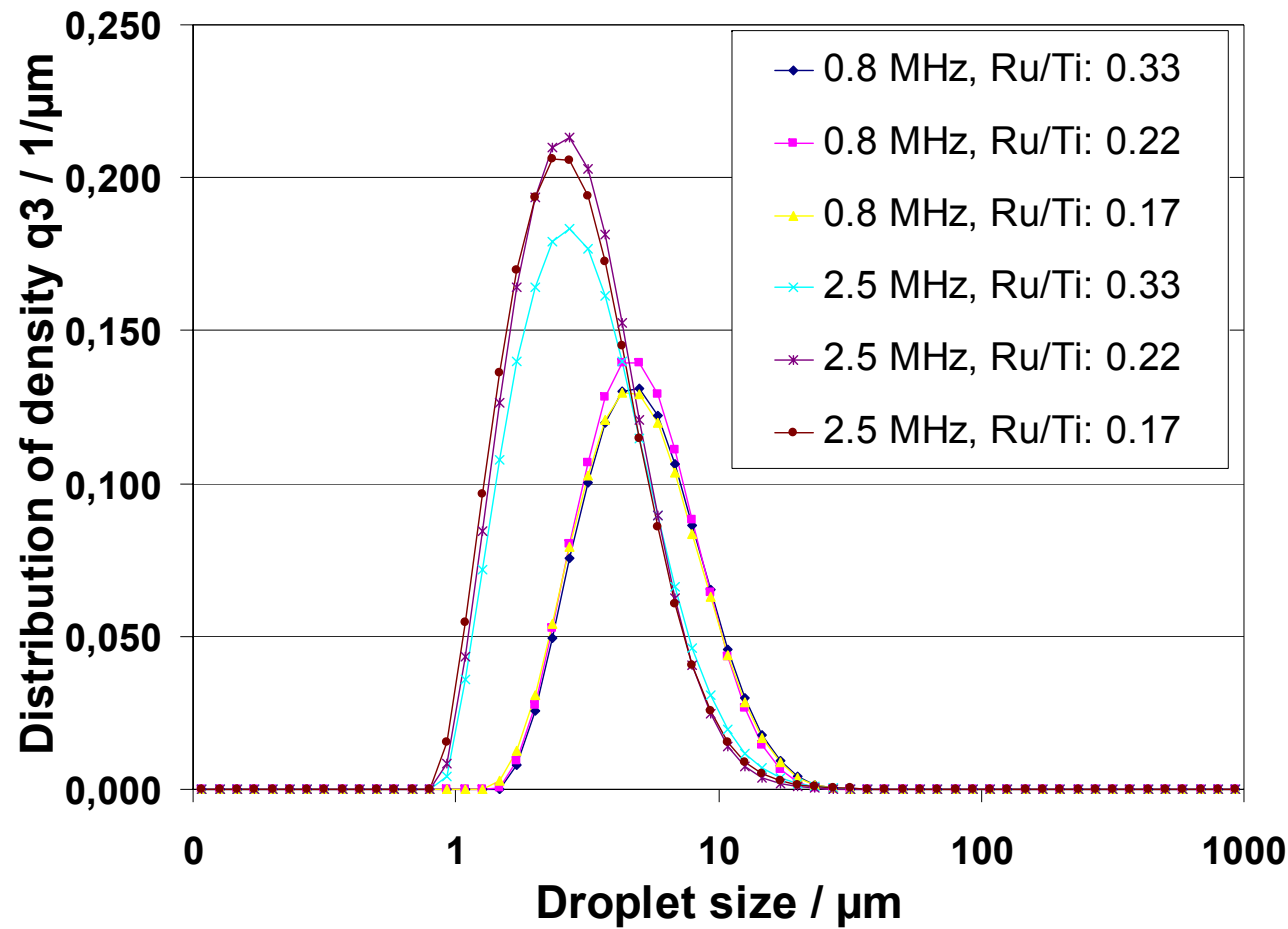
Measurement of droplet size distribution for water solution



f= 0.8 MHz
 $D_{50} = 7.88 - 9.53 \mu\text{m}$
f= 2.5 MHz
 $D_{50} = 6.12 - 6.56 \mu\text{m}$

- Increase of frequency from 0.8 to 2.5 MHz decreases the aerosol droplet.
- The change of flow rate does not influence on aerosol droplet size.

Measurement of droplet size distribution for Ru/Ti Solution



$f = 0.8 \text{ MHz}$
 $D_{50} = 6.28 - 6.52 \mu\text{m}$
 $f = 2.5 \text{ MHz}$
 $D_{50} = 3.86 - 4.32 \mu\text{m}$

- Increase of frequency from 0.8 MHz to 2.5 MHz decreases the aerosol droplet.
- The change of Ru/Ti mass ratio does not influence on droplet size.

Calculated aerosol droplet size

$$D_{\text{droplet}} = 0.34 \cdot \left(\frac{8\pi \cdot \gamma}{\rho \cdot f^2} \right)^{\frac{1}{3}}$$

Peskin, Raco (1963) J.Acoust.Sci

D diameter of aerosol droplet [μm]
 γ surface tension of liquid [N/m]
 ρ density of liquid [g/cm^3]
f frequency of ultrasound [$1/\text{s}$]

calculated values (water)
f=0.8 MHz, D=4.79 μm
f=2.5 MHz, D=2.26 μm

for water solution:

$$\gamma = 72,9 \cdot 10^{-3} \text{ N/m}; \rho = 1 \text{ g/cm}^3$$

calculated values (real solution)
f=0.8 MHz, D=3.83 μm
f=2.5 MHz, D=1.81 μm

for real solution (measured values)

$$\gamma = 37,2 \cdot 10^{-3} \text{ N/m}; \rho = 1,01 \text{ g/cm}^3$$

Measured Values (real solution):

f=0.8 MHz $D_{50} = 6.28 - 6.52 \mu\text{m}$
f=2.5 MHz $D_{50} = 3.86 - 4.32 \mu\text{m}$

big importance of the measured values of precursor in order to precise determine of aerosol droplet

Required cooperation with IPC, RWTH and KIT, Karlsruhe

IPC, RWTH Aachen University

- Characterisation of nanoparticles: Morphology, particle size, porosity, chemical composition (REM, TEM, EDS, XRD, FIB)
- New mechanism for core-shell formation of different nanosized particles

KIT, Karlsruhe

New measurement of droplet size for ultrasonic generator with 3 different ultrasonic transducer of 2.5 MHz



Conclusion

- first measurement of aerosol droplet produced by ultrasonic spray pyrolysis performed by laser diffraction
- difference between theoretically and obtained droplet size
- increase of ultrasonic frequency decreases aerosol droplet size
- no influence on the droplet size by change of Ru/Ti mass ratio and flow rate of nitrogen
- Decrease of surface tension of real solution decreases of aerosol droplet size
- The obtained values of aerosol sizes might help in better explanation of final obtained nanosized particle of $\text{RuO}_2/\text{TiO}_2$

Thank you very much for your attention

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