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Dual Cocatalytic Nanohybrids [(Rutile)TiO_2/Au/(Rutile)RuO_2] and [(Anatase)TiO_2/Au/(Rutile)RuO_2]; Switch between Strong Oxide Support Interaction and Heterojunction for overall Water Splitting

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GSPEE2023
2nd Global Summit on Power and Energy Engineering
March 20-22 Rome, Italy

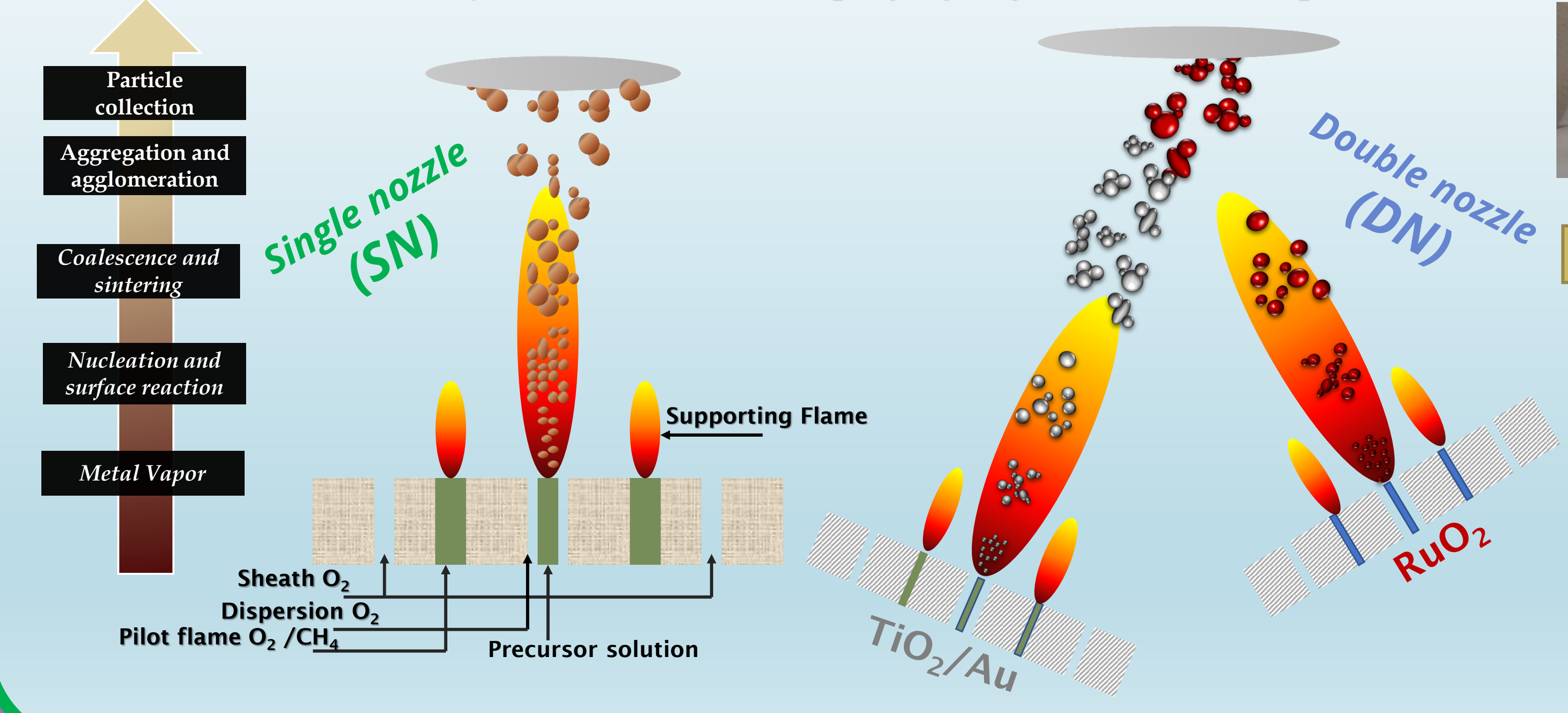
Lab Phys-Chem Materials & Environment

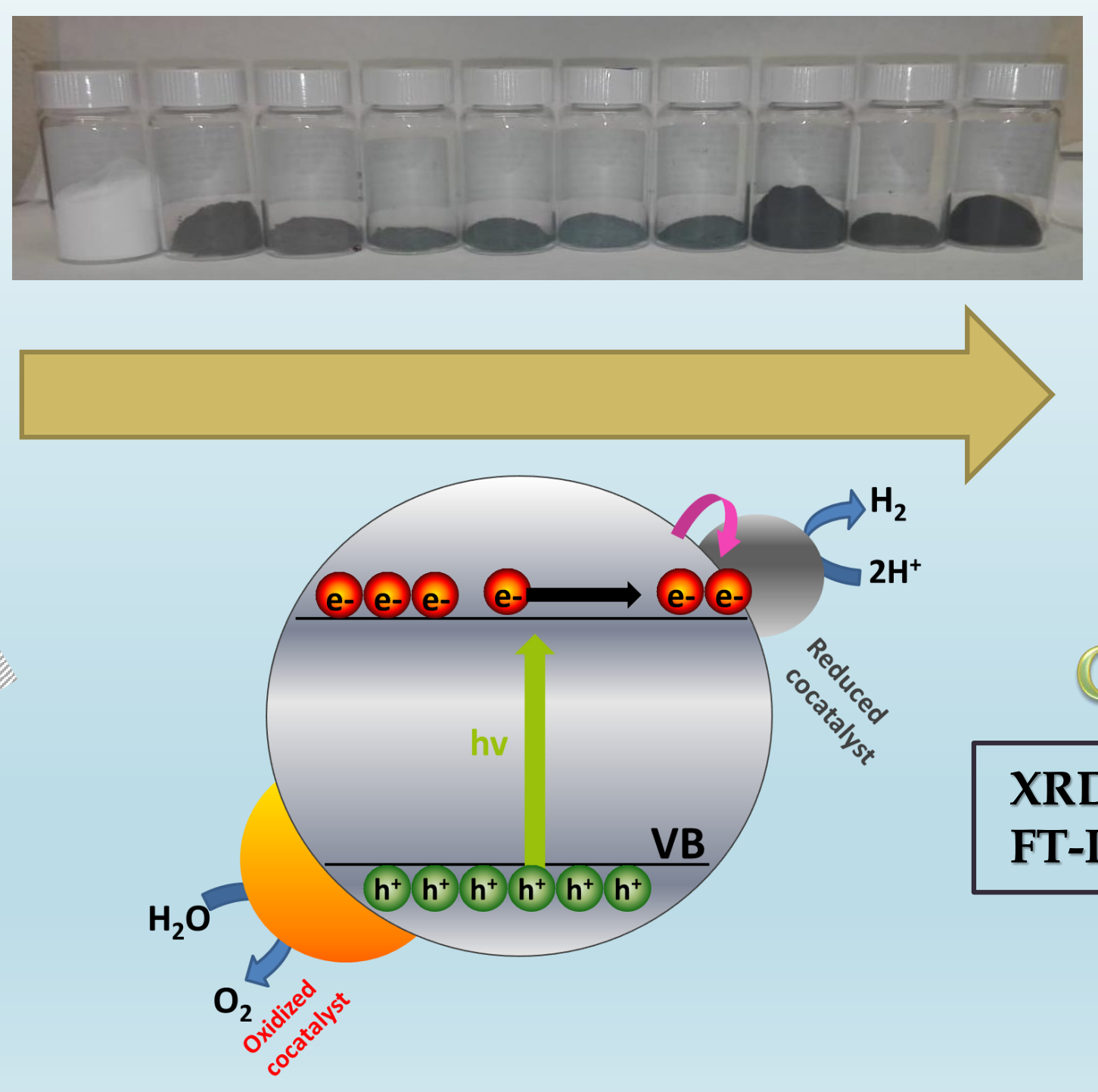
Introduction

Photocatalytic hydrogen (***H_2***) and oxygen (***O_2***) generation using semiconducting materials is regarded as the most promising approach for solar energy conversion and the framework for future renewable energy supplies. Among various metal oxide semiconductors, ***TiO_2*** has been extensively employed as a photocatalyst because to its comparatively high photocatalytic activity, stability into photochemical corrosion, low cost and nontoxicity. But it has various limitations, with the most important being the fast electron (e^-)- hole (h^+) recombination, and large band gap (3.2-3.0 eV), establishing a non – solar light semiconductor. Surface modification and bang gap engineering could be very important strategies for improving the overall photocatalytic activity from the TiO_2. To this direction, numerous studies include the loading of noble metals, the ion doping, or a junction with another metal oxide. heterojunction with another semiconductor (RuO_2, IrO_2, NiO_2), could be an another successful strategy. Among them ***Ruthenium Oxide (IV) RuO_2***, which belongs to the family of the d-band transition-metal oxides with a rutile-like structure exhibits a wide range of characteristics. Its chemical stability, electrical (metallic) conductivity, and outstanding diffusion barrier properties make it an ideal diffusion barrier material. Consequently, a successful cocatalyst deposition technique onto TiO_2 must satisfy the following requirements: (**1**) high dispersion capacity onto the TiO_2 surface, (**2**) optimal interfacing of rutile/anatase ratio and (**3**) stable adsorption configurations of cocatalyst-catalyst through lattice matching. Some synthesis techniques have satisfied the three conditions, despite their disadvantages of being multistep, time-consuming, or meeting just a portion of the three criteria. Using ***Single Nozzle (SN)*** and ***Double Nozzle (DN) Flame Spray Pyrolysis (FSP)*** technology, we have synthesized with different loadings, ***dual cocatalysts [(R)TiO2/Au/(R)RuO_2]*** and ***[(A)TiO_2/Au/(R)RuO_2]***, (where **R=Rutile** and **A=Anatase**) nanoparticles in a single step. As it proved from characterization techniques, TEM microscopy and EPR study the ***DN [TiO_2/Au/RuO_2]*** nanohybrids promotes the construction of ***Strong Oxide Support Interactions (SOSI)***.

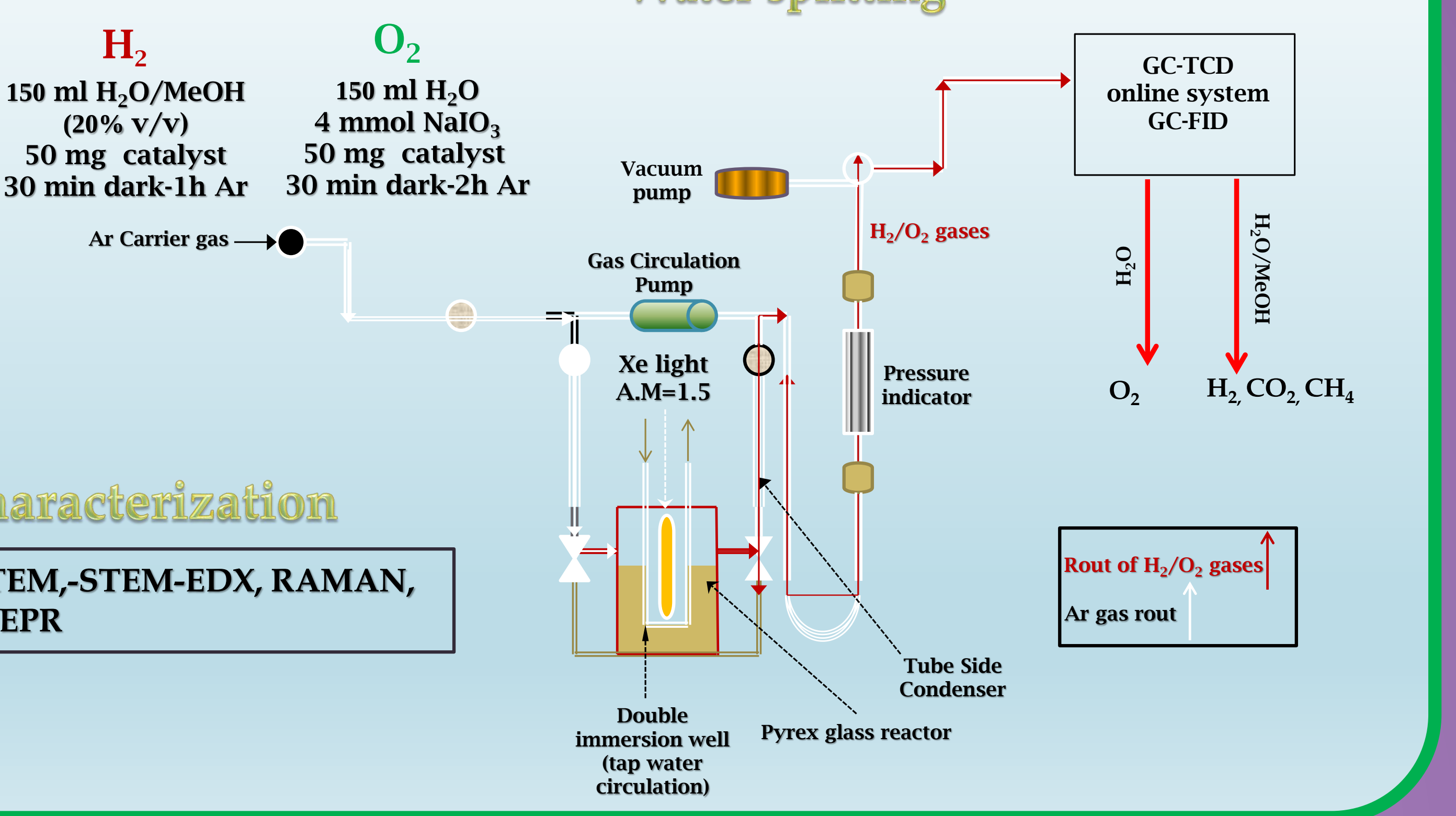
Experimental Procedure

Production of Nanoheterojunctions via Flame Spray Pyrolysis (FSP) technique





Water splitting



H_2
150 ml H_2O/MeOH
(20% v/v)
50 mg catalyst
30 min dark-1h Ar

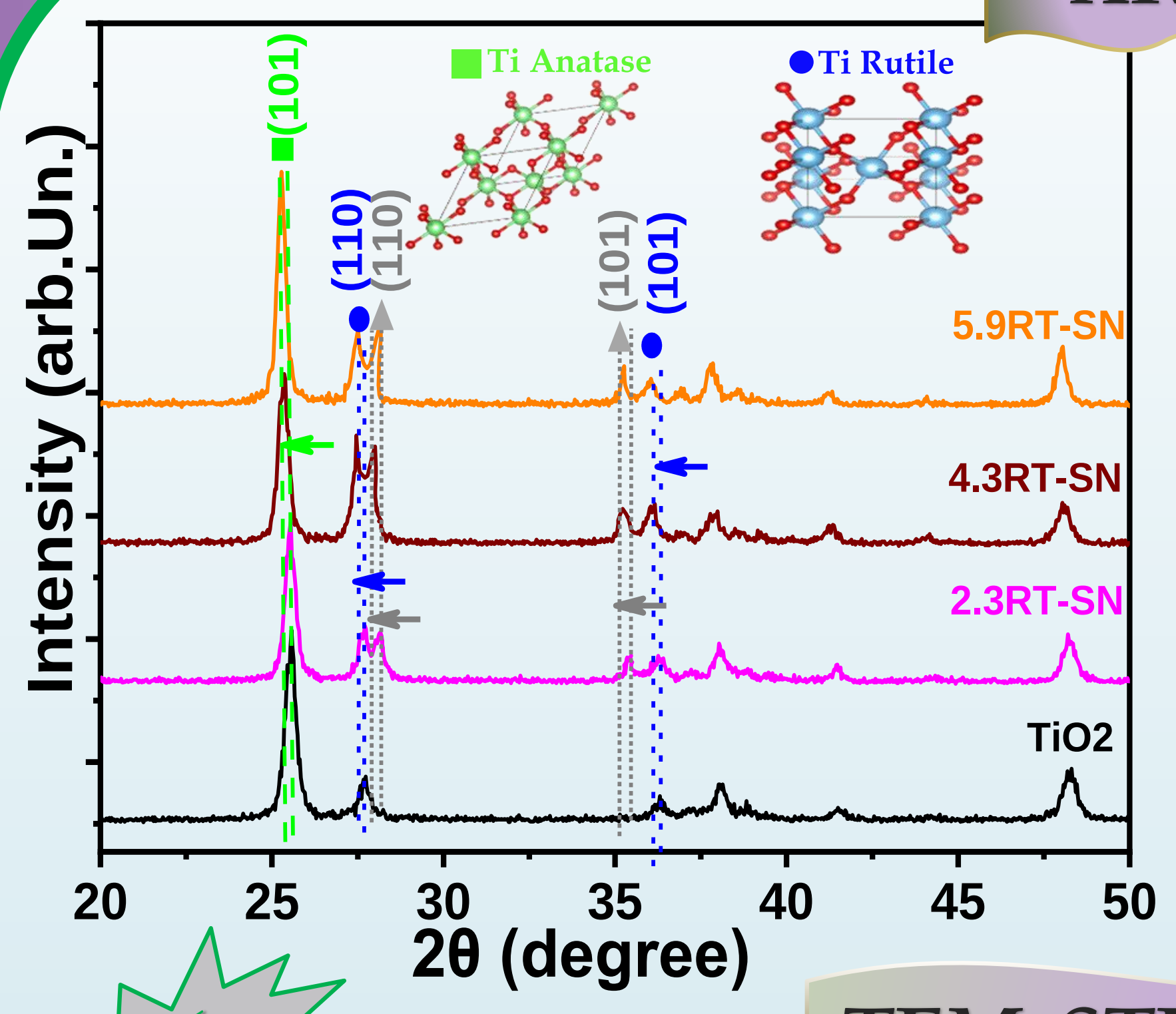
O_2
150 ml H_2O
4 mmol $NaIO_3$
50 mg catalyst
30 min dark-2h Ar

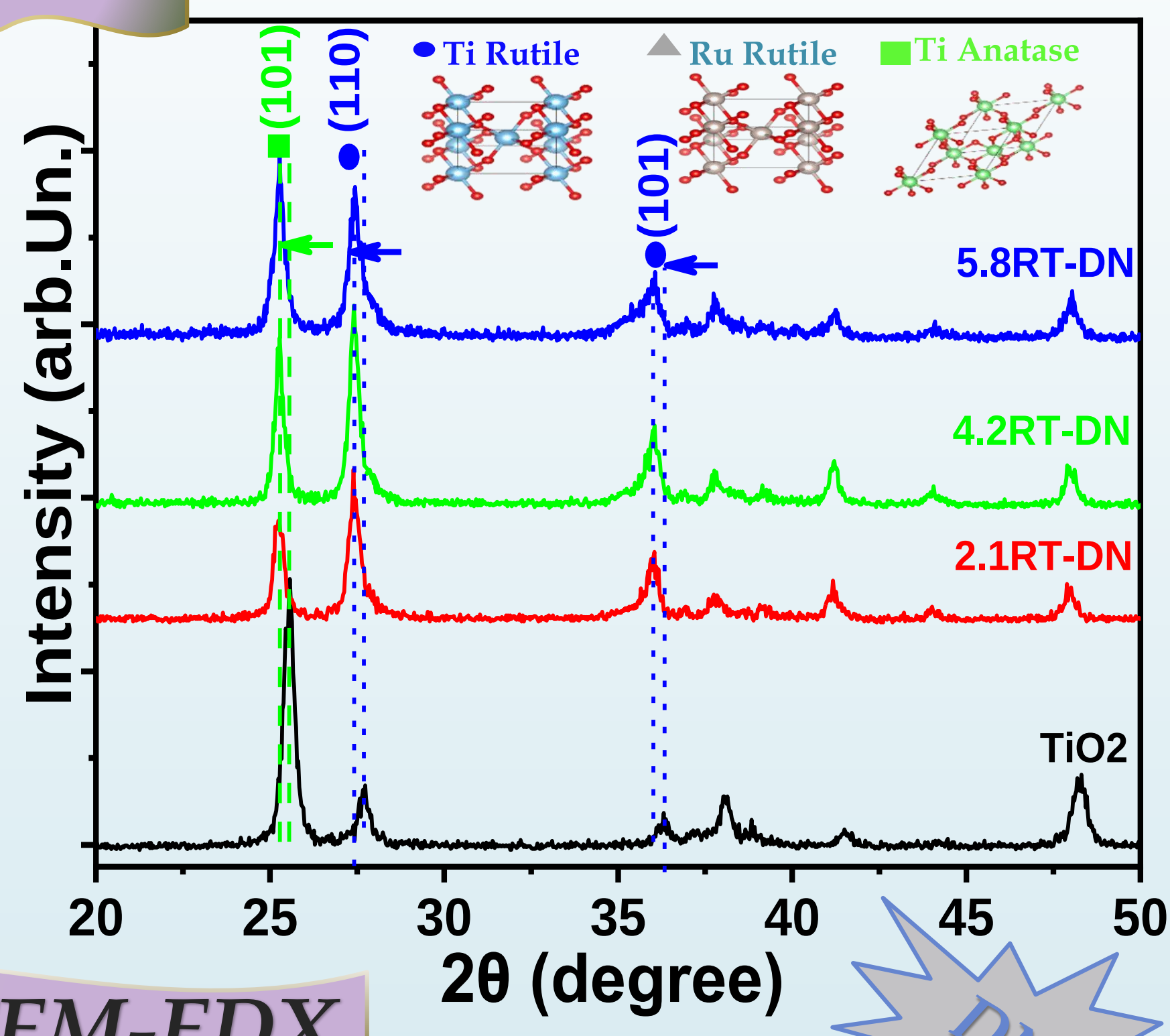
Characterization

XRD, TEM,-STEM-EDX, RAMAN, FT-IR, EPR

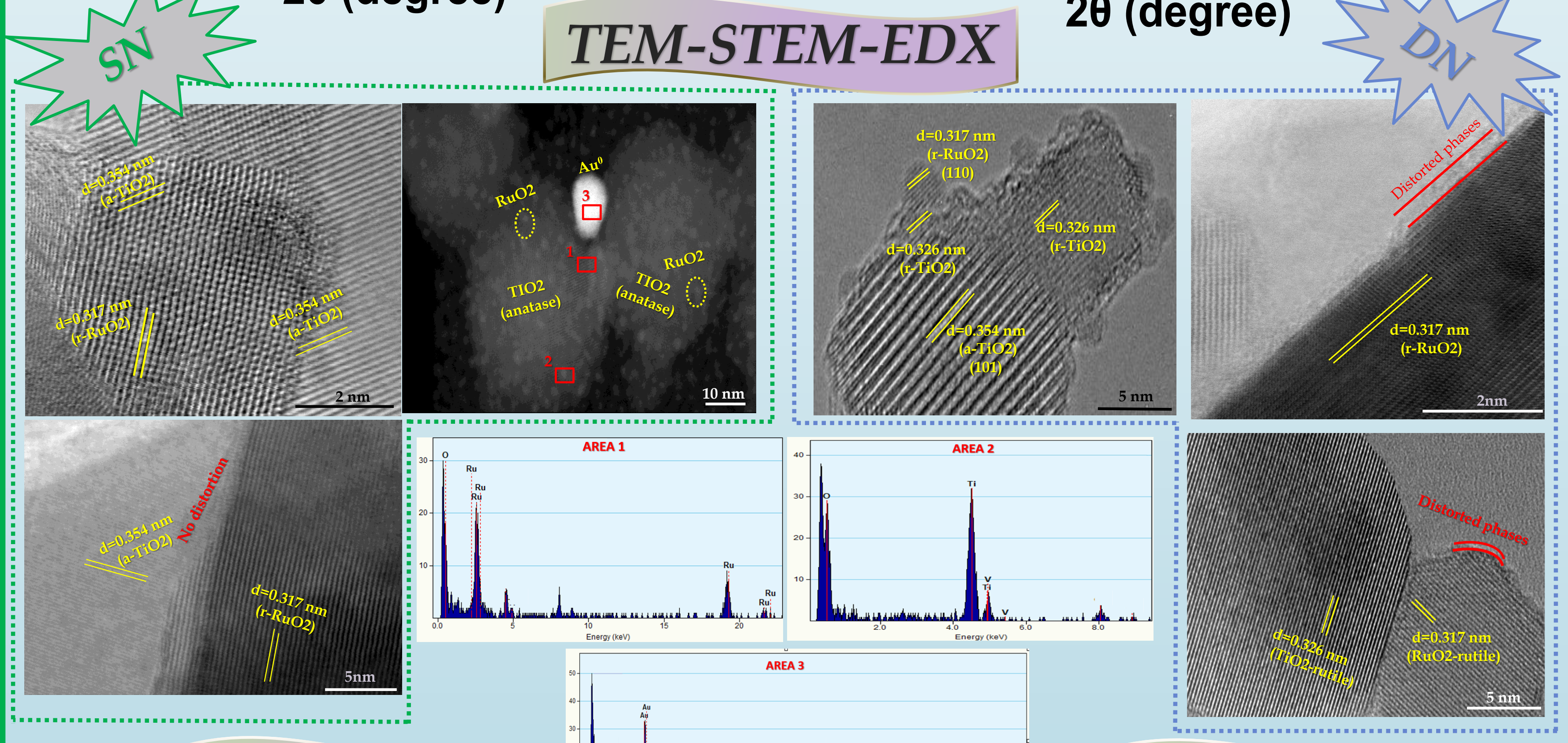
Results

XRD

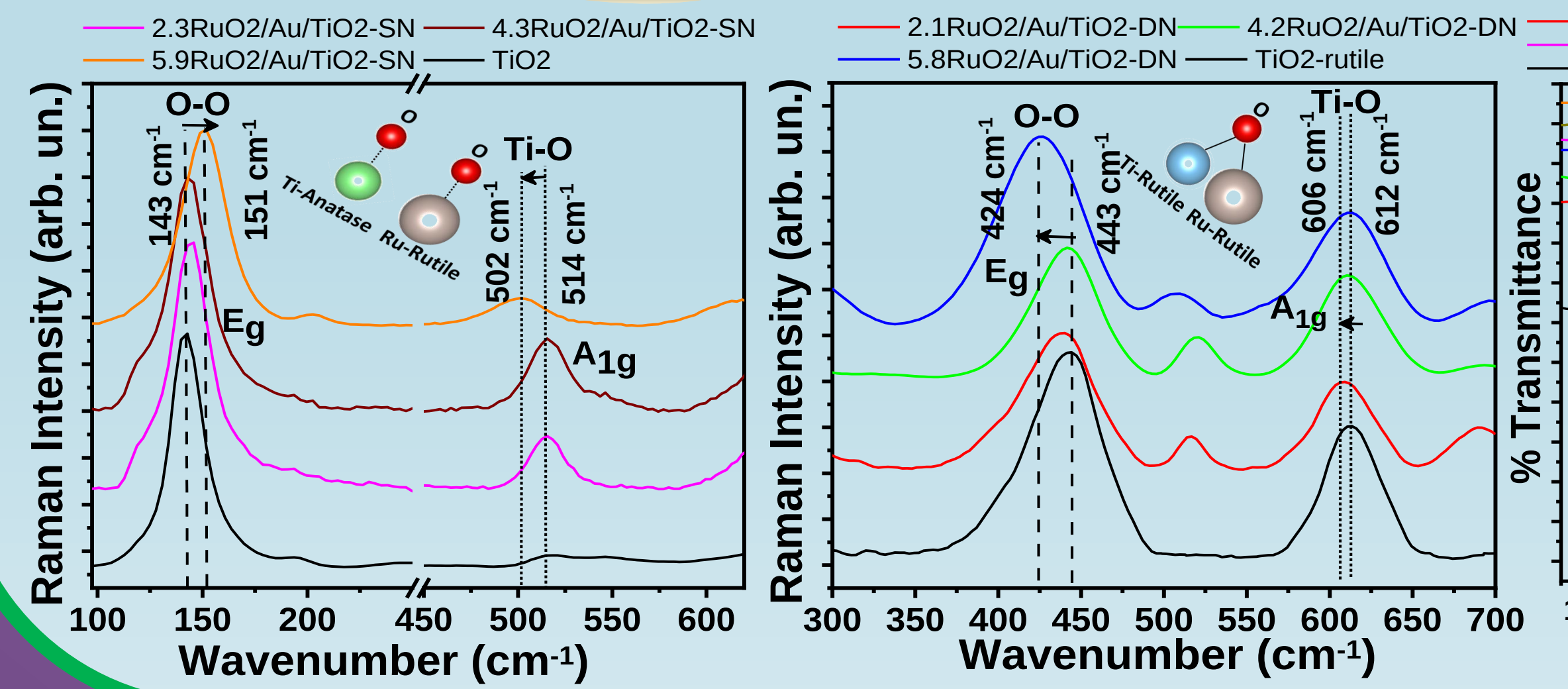




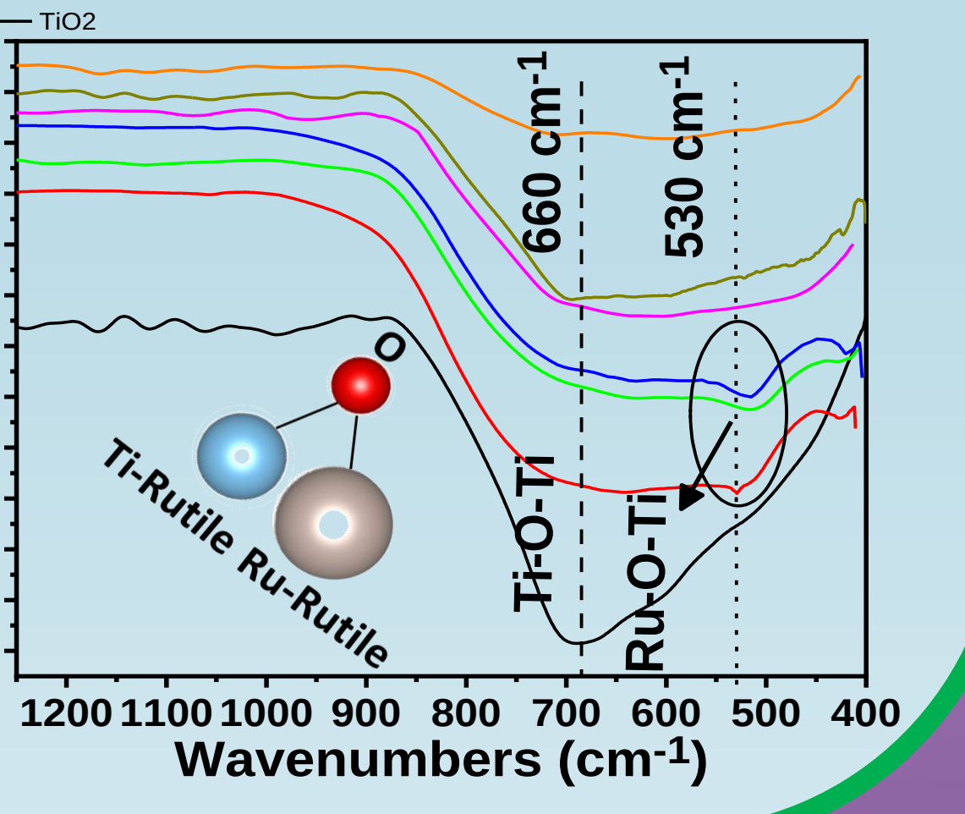
TEM-STEM-EDX



Raman

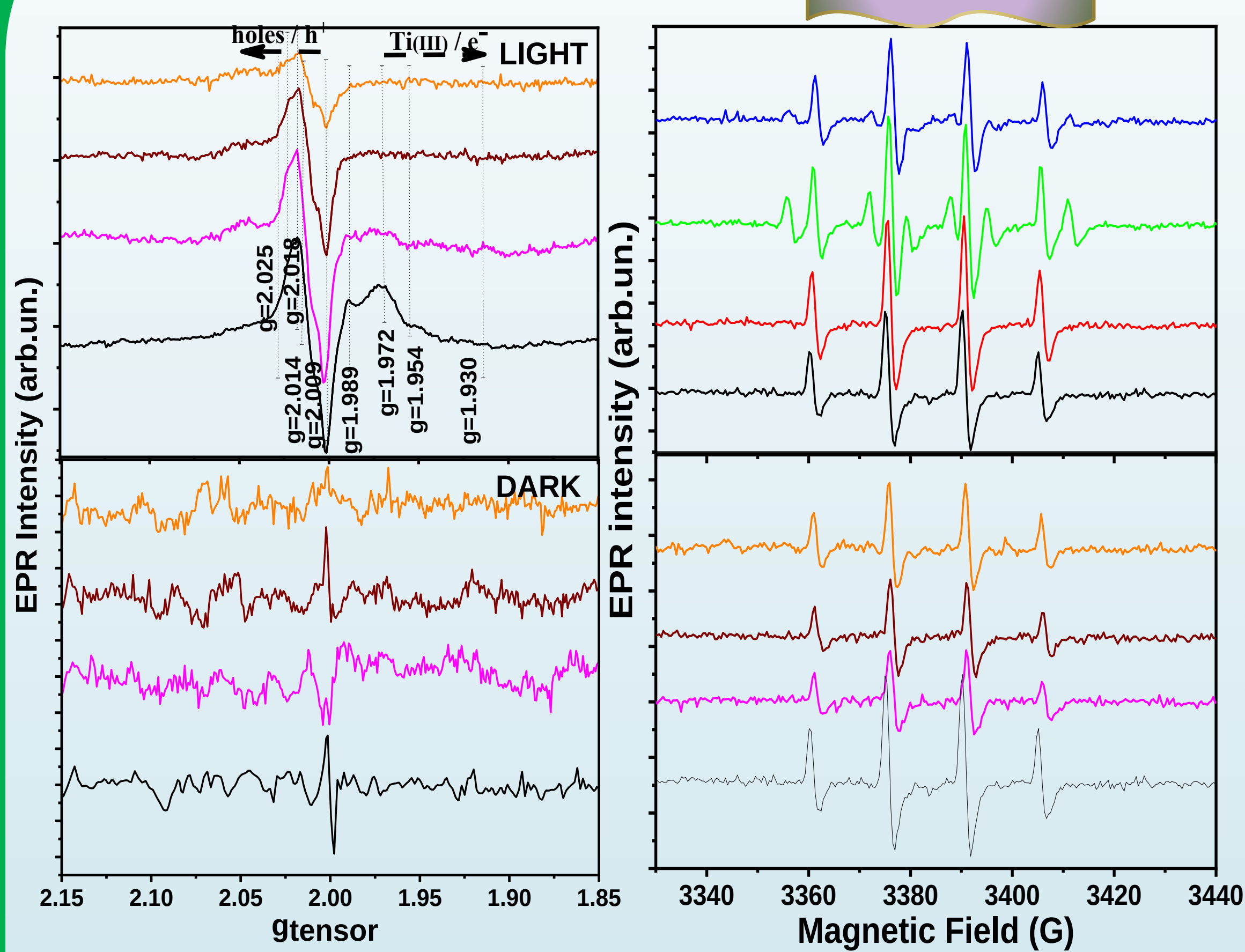


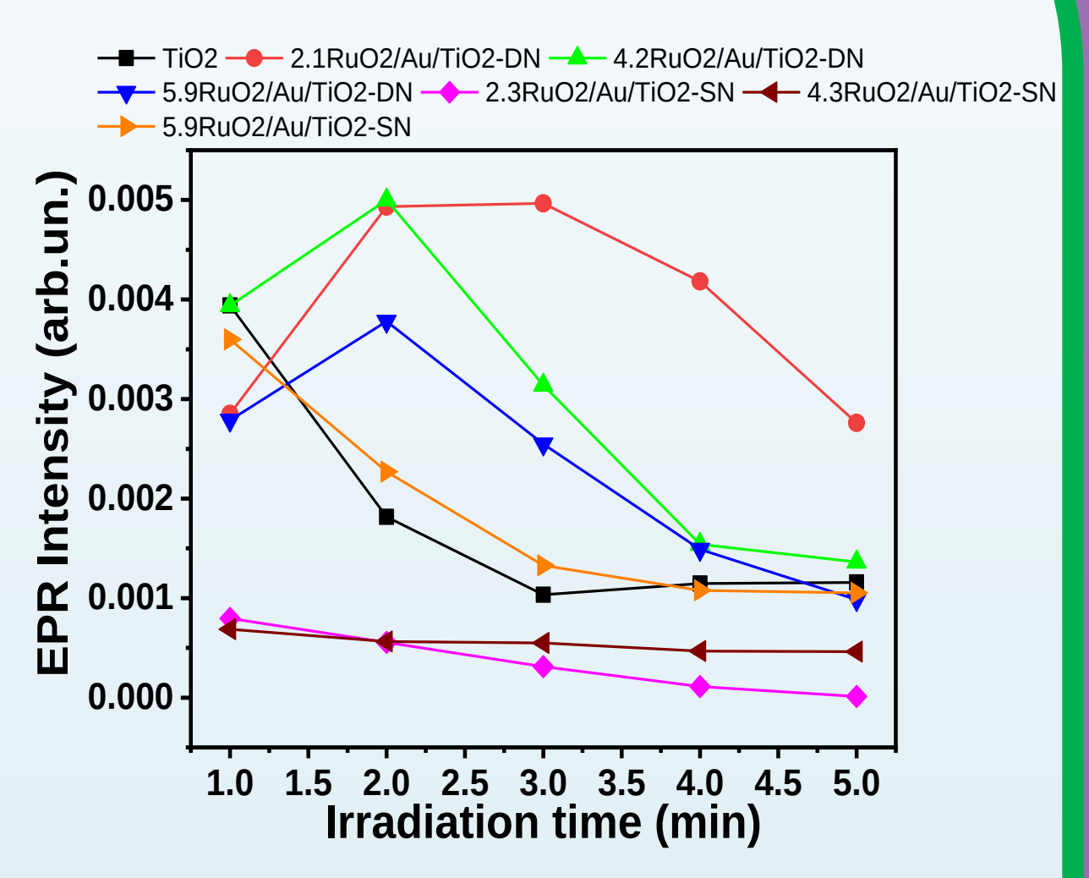
FT-IR



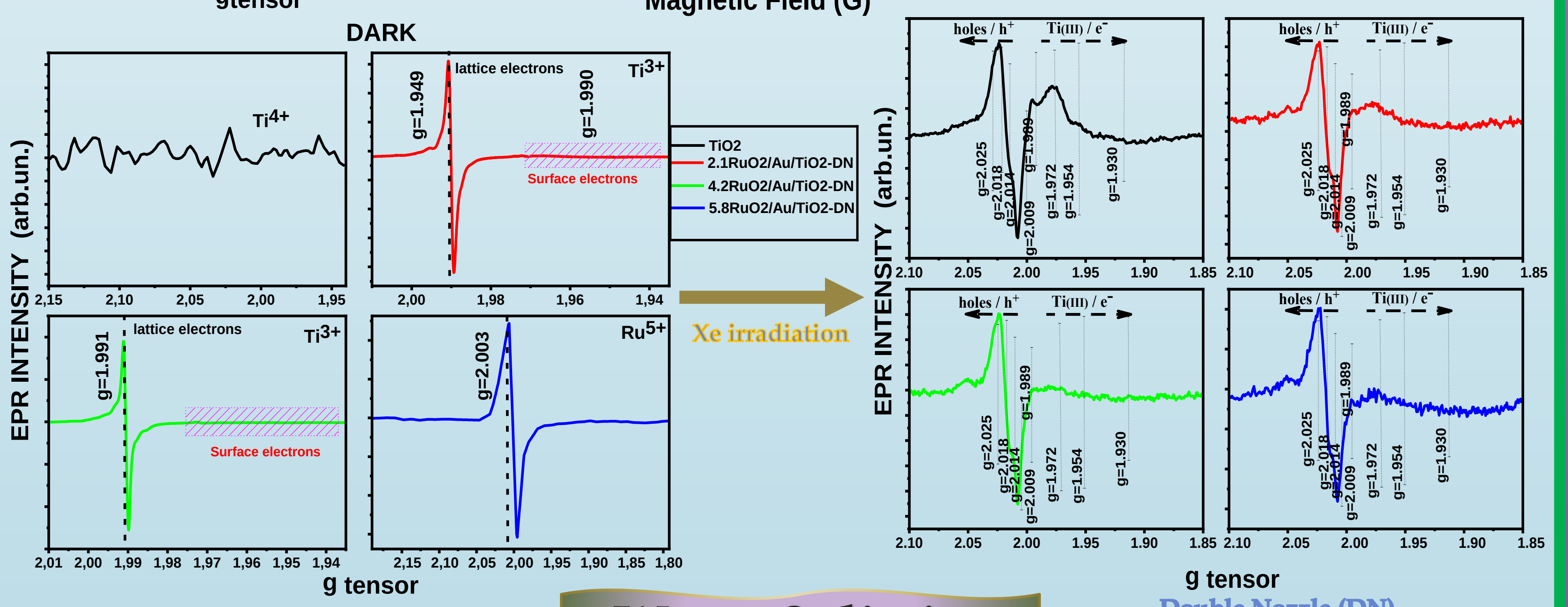
Results

EPR





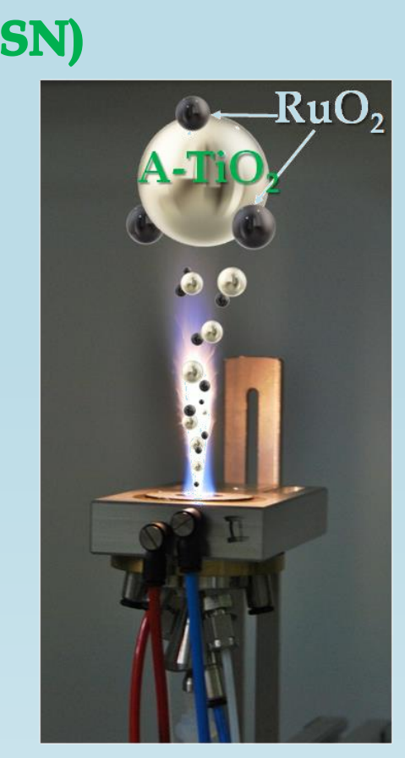
- Ti^{3+} in the dark (lattice and surface electrons)
- In the case of high loading of Ru, they are dominating Ru^{5+} species in the dark. Upon illumination they are disappeared and creating Ti^{3+} paramagnetic species. $Ru^{5+} + e^- \rightarrow Ru^{4+}$ (diamagnetic)



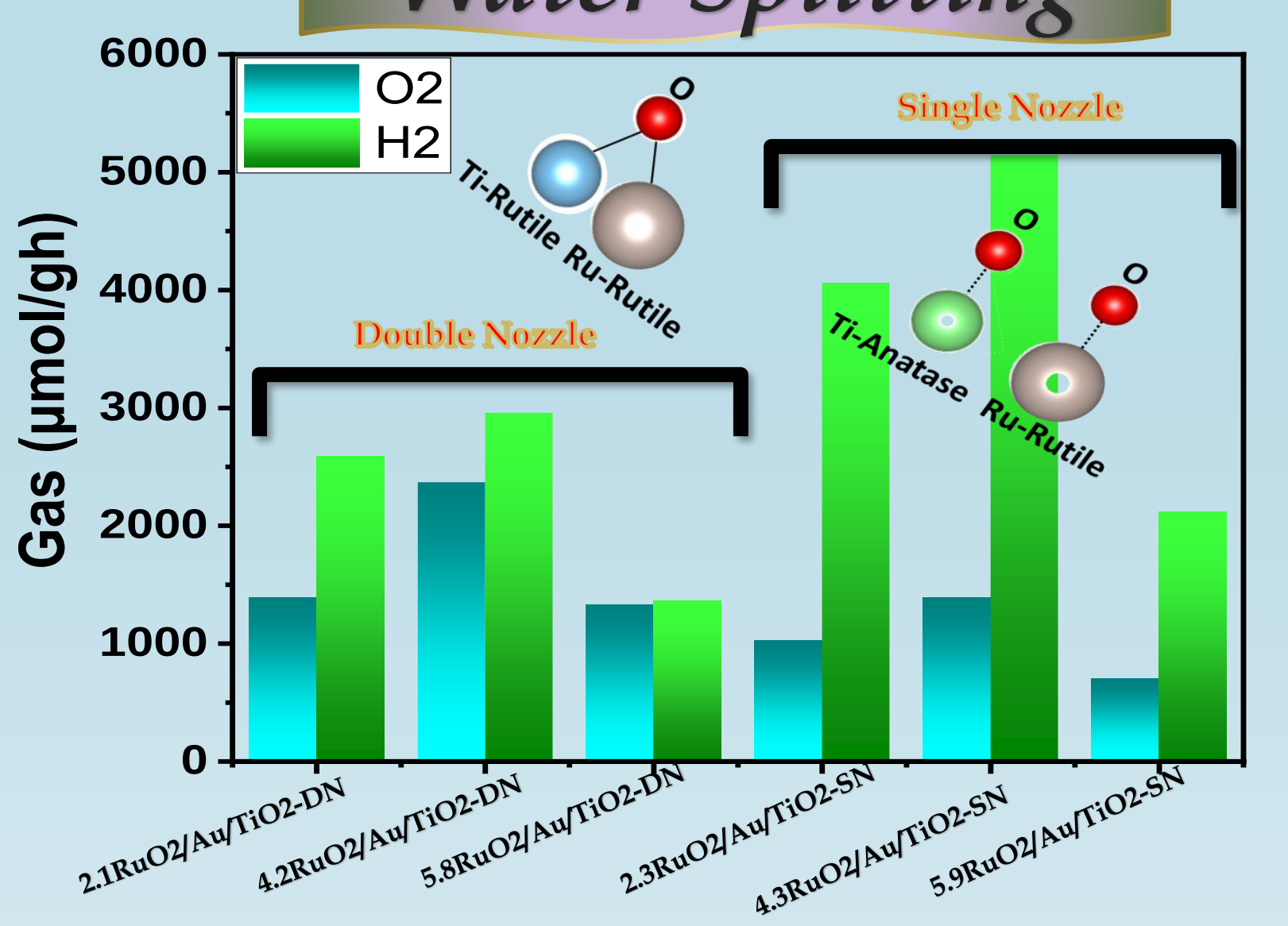
Water Splitting

Single Nozzle (SN)

Heterojunction



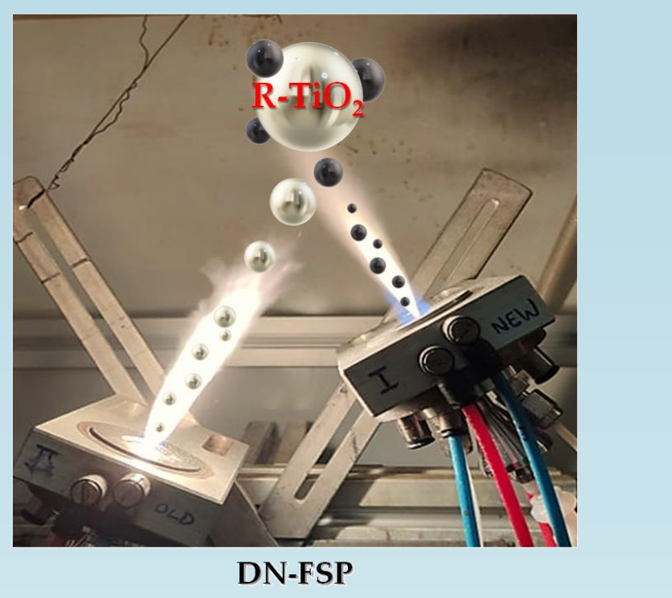
SN-FSP
TiO_2 (Anatase)-RuO_2



g tensor

Double Nozzle (DN)

Strong Oxide Support Interaction (SOSI)



DN-FSP
TiO_2 (Rutile)-RuO_2

Conclusions

- Nanoheterostructures [TiO_2/Au/RuO_2] with different loadings were synthesized using Single Nozzle (SN) and Double Nozzle (DN) FSP technology.
- SN [TiO_2/Au/RuO_2] have higher percentage of anatase phase with higher crystal size (as it is proved by TEM and XRD). RuO2 is absent in XRD patterns in the case of DN [TiO_2/Au/RuO_2]. This explained because of smaller size and high dispersion capacity (STEM images)
- DN favors the formation of Rutile phase (XRD and Raman), and lattice distortion (TEM and EPR where it appears the characteristic Ti^{3+} signal)
- DN [TiO_2/Au/RuO_2] favors the Strong Oxide Support Interaction (SOSI) phenomenon (Ti^{3+} signal, distorted phases around RuO_2 and Ti-O-Ru bond formation (530 cm^{-1}) from FT-IR)
- SN 4.3[TiO_2/Au/RuO_2] produces approx. 5000 μmol$g^{-1}h^{-1}$ H_2, while DN 4.3[TiO_2/Au/RuO_2] produces 1250 μmol$g^{-1}h^{-1}$ O_2. The best H_2 and O_2 photocatalyst is coming from SN and DN-FSP technology accordingly (higher population of OH radicals it is manifested in the case of DN, boosting the O_2 evolution. Instead, SN [TiO_2/Au/RuO_2] has higher percentage of surface electrons.

References

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Acknowledgments

This research was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I) under the "First call for H.F.R.I. Research projects to support Faculty members and Researchers and the procurement of high-cost research equipment grant" (Project number: 1888)

H.F.R.I.
Hellenic Foundation for Research & Innovation