Engineering of flame-made plasmonic-semiconducting nanocatalysts: A study of the photo-induced carrier dynamics and interfacial electron transfer

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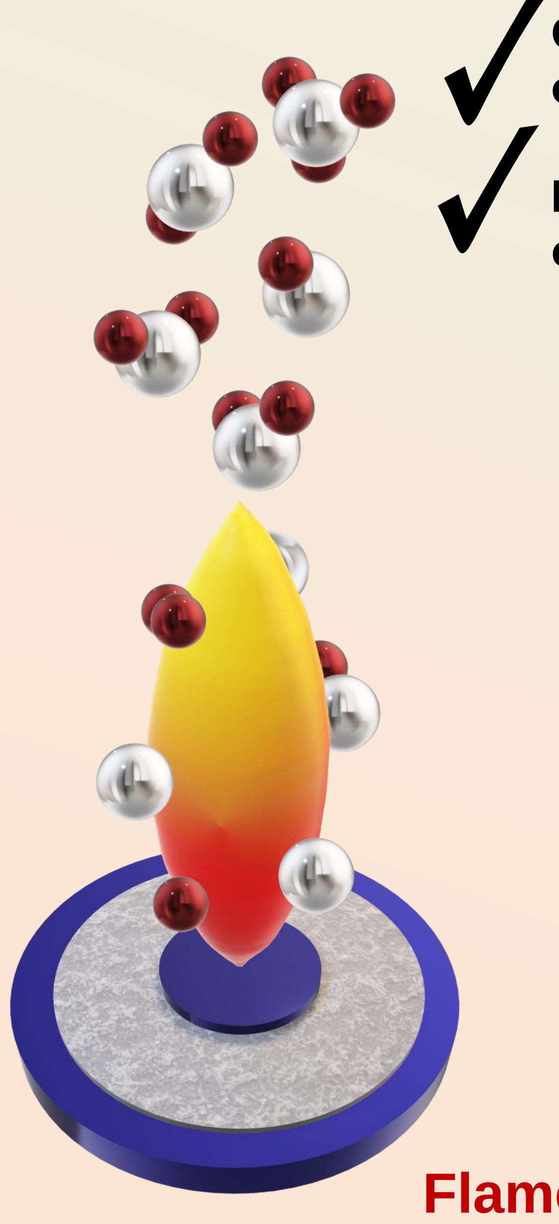
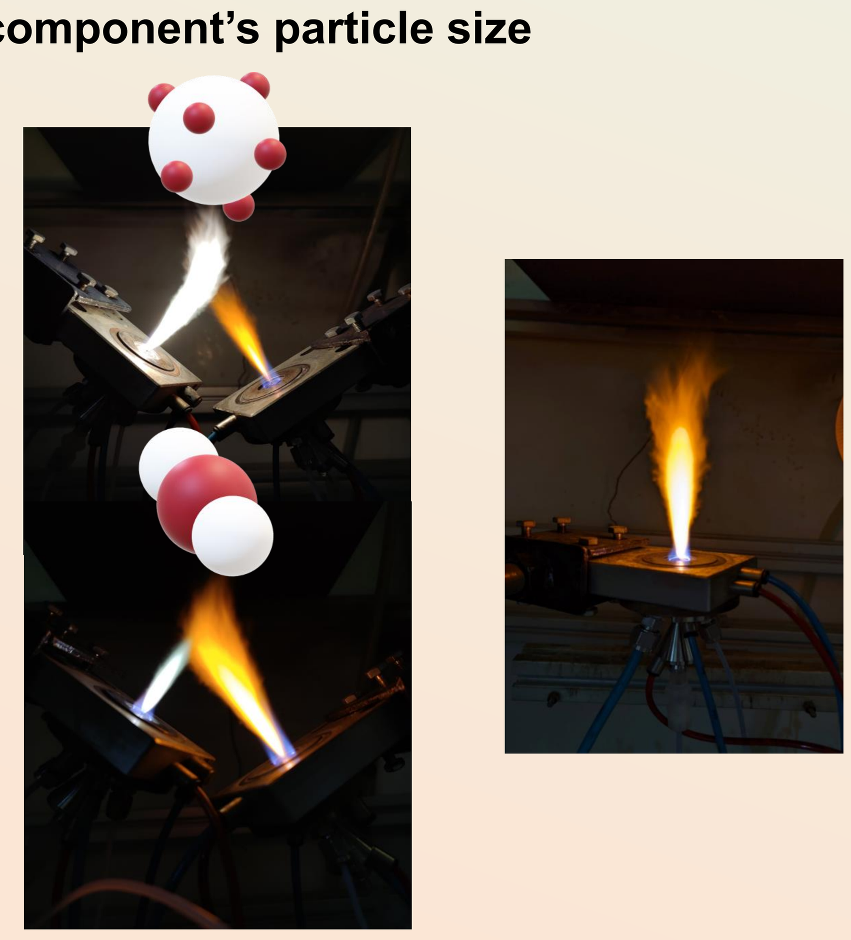
MOTIVATION

Harvesting solar energy remains the most attractive route towards energy independency and climate neutrality employing particulate photocatalysts. In this regard, plasmonic photocatalysts have been emerged as an innovative pathway promising efficient sunlight energy conversion into chemical activity and amplifying challenging reactions, such as H_2 production and CO_2 reduction. When coupled to a semiconductor, the sufficient generation and injection of the plasmon-induced, highly energetic "hot" electrons necessitate the engineering and optimization of the plasmonic/semiconductor interface so that enhanced performance can be achieved.

DESIGN OF "BLACK" Ag/TiO_2

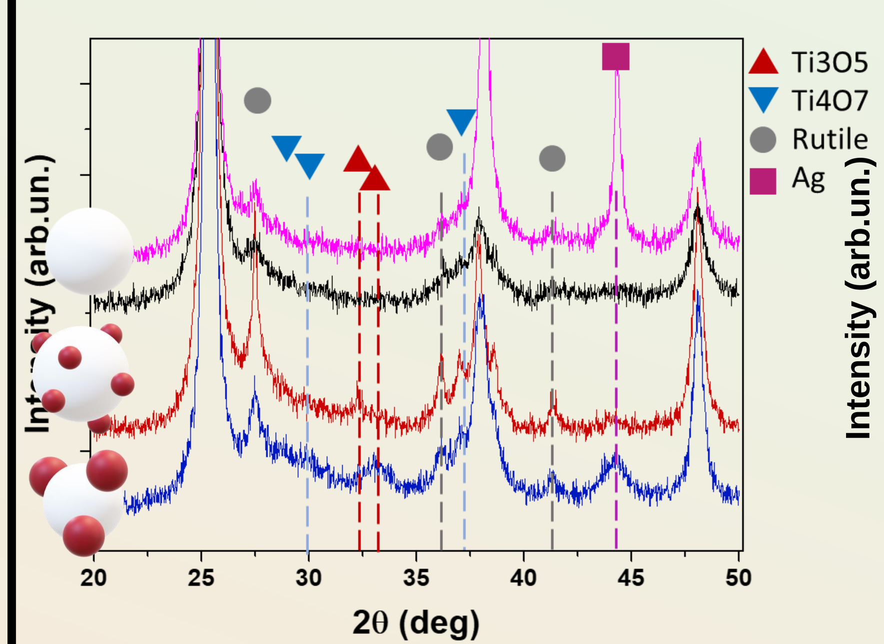
- ✓ One step formation of Ag/TiO_2 heterostructure
- ✓ Independent control of each component's particle size



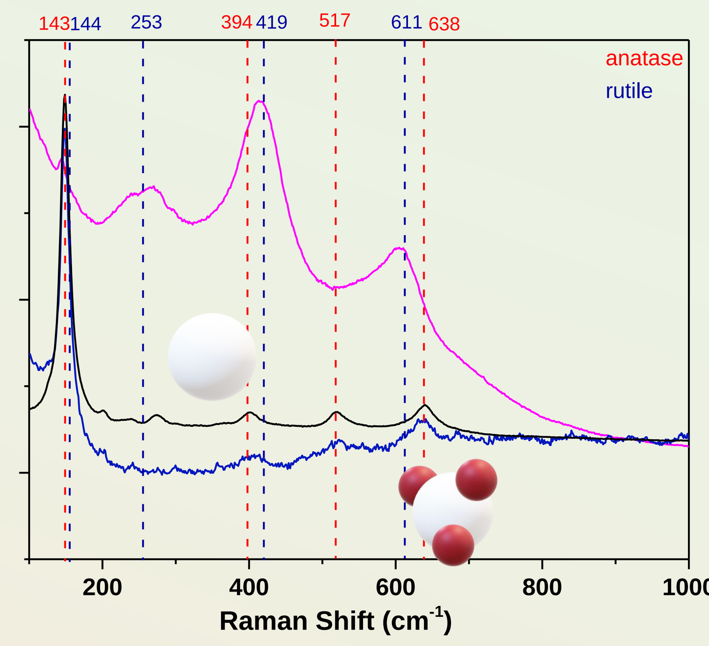


Flame Spray Pyrolysis

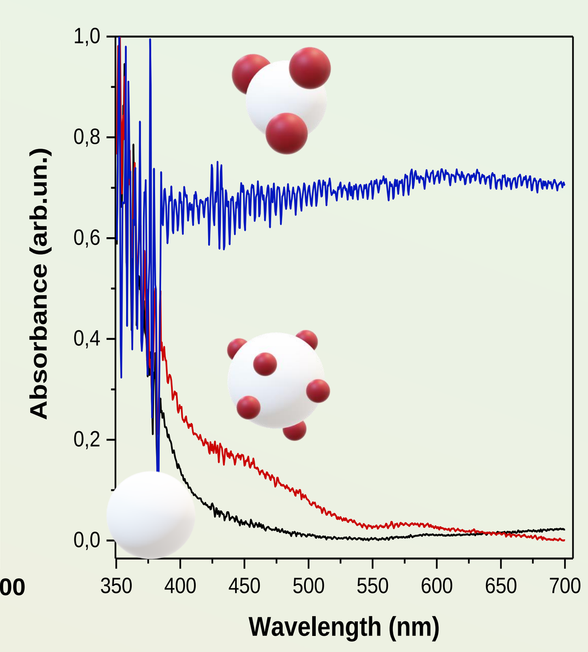
FORMATION OF MAGNELI LAYERS IN FLAMES



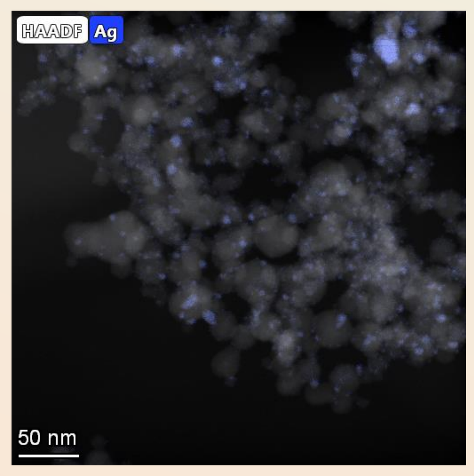
Formation of TiOx suboxides (Magneli)



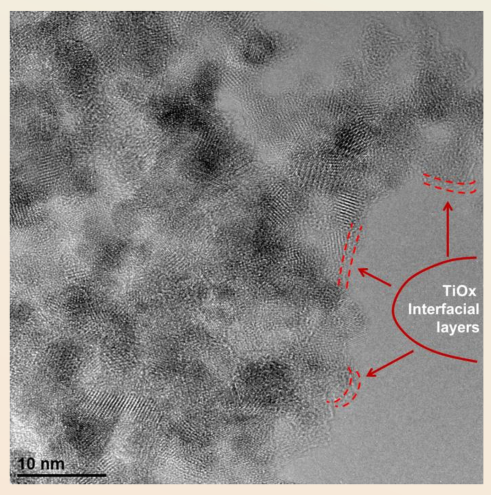
Lattice distortion
Ti-O bond stretching



LSPR damping
Visible-light absorption



Controlled Ag size and dispersion

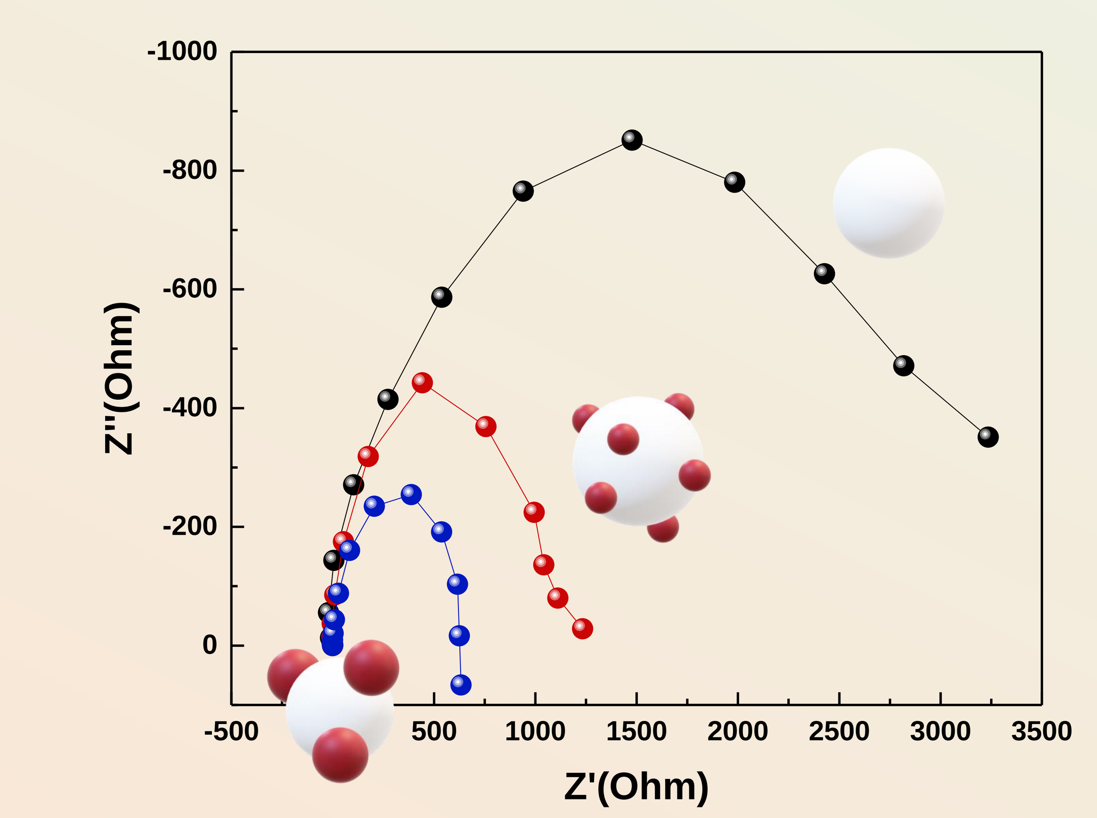


The interfacial TiOx suboxide layer (Magneli) encapsulates Ag.

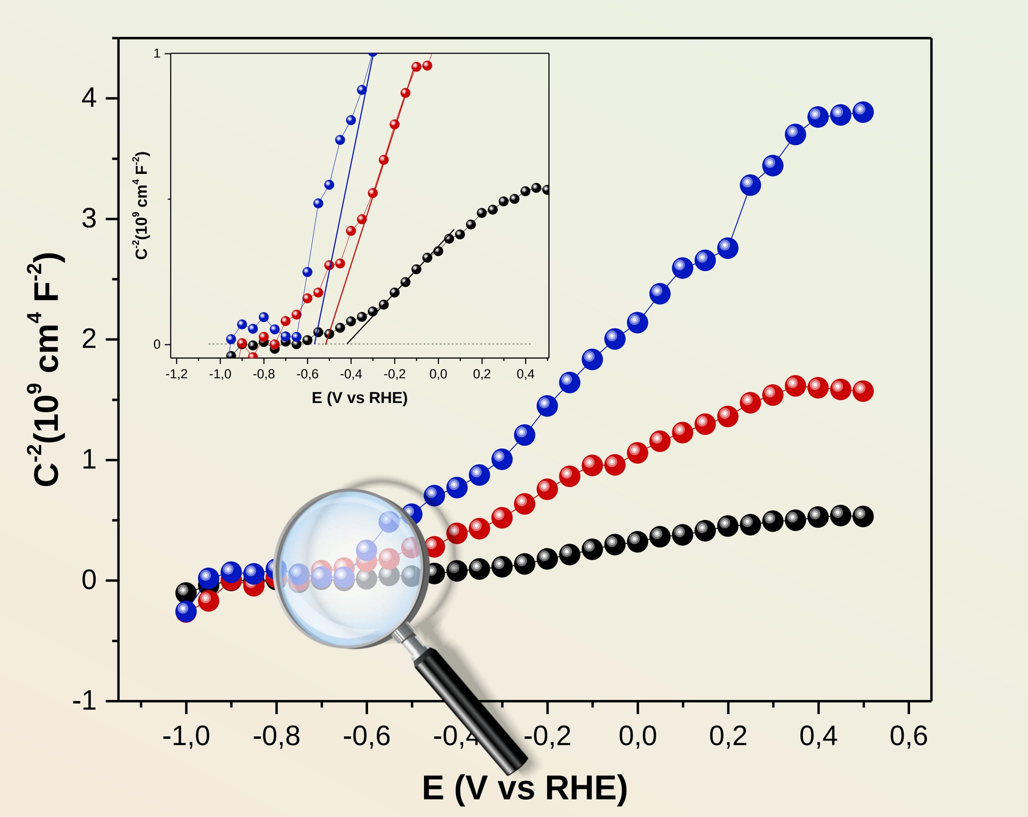
Both large TiO_2 & Ag particles promote the presence of Magneli nano-islands.

Rutile and Magneli phases are in contradiction in flame synthesis.

PHOTO-INDUCED CARRIER DYNAMICS

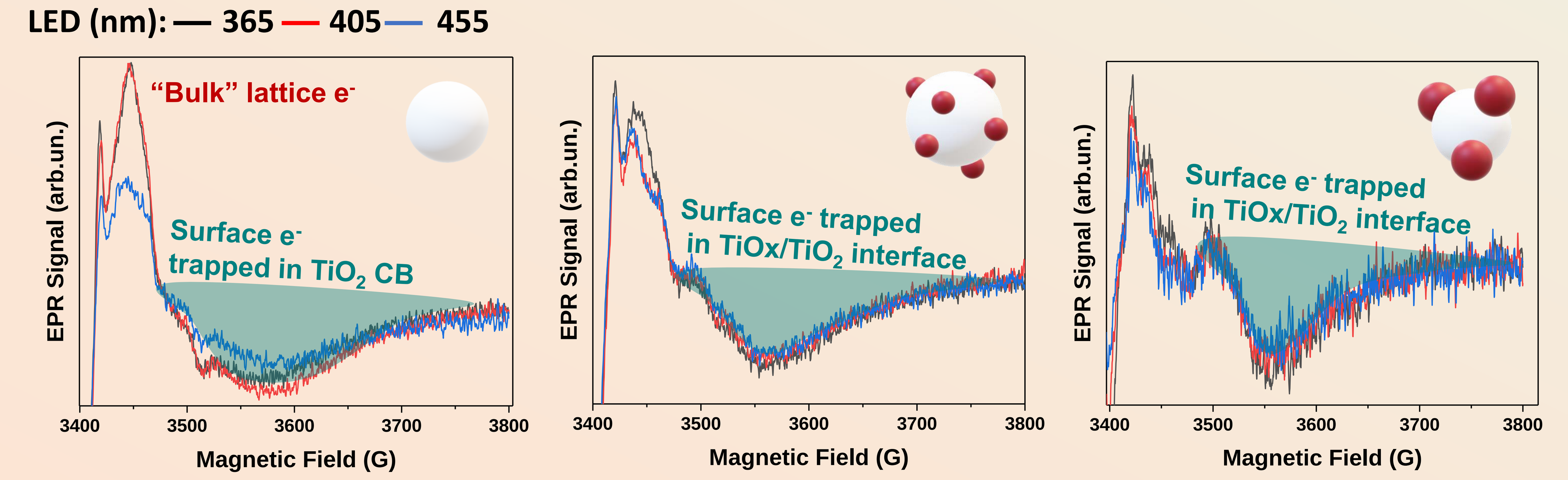


Increased Ag Size – Enhanced carrier mobility
Magneli layer can act as semi-metal.



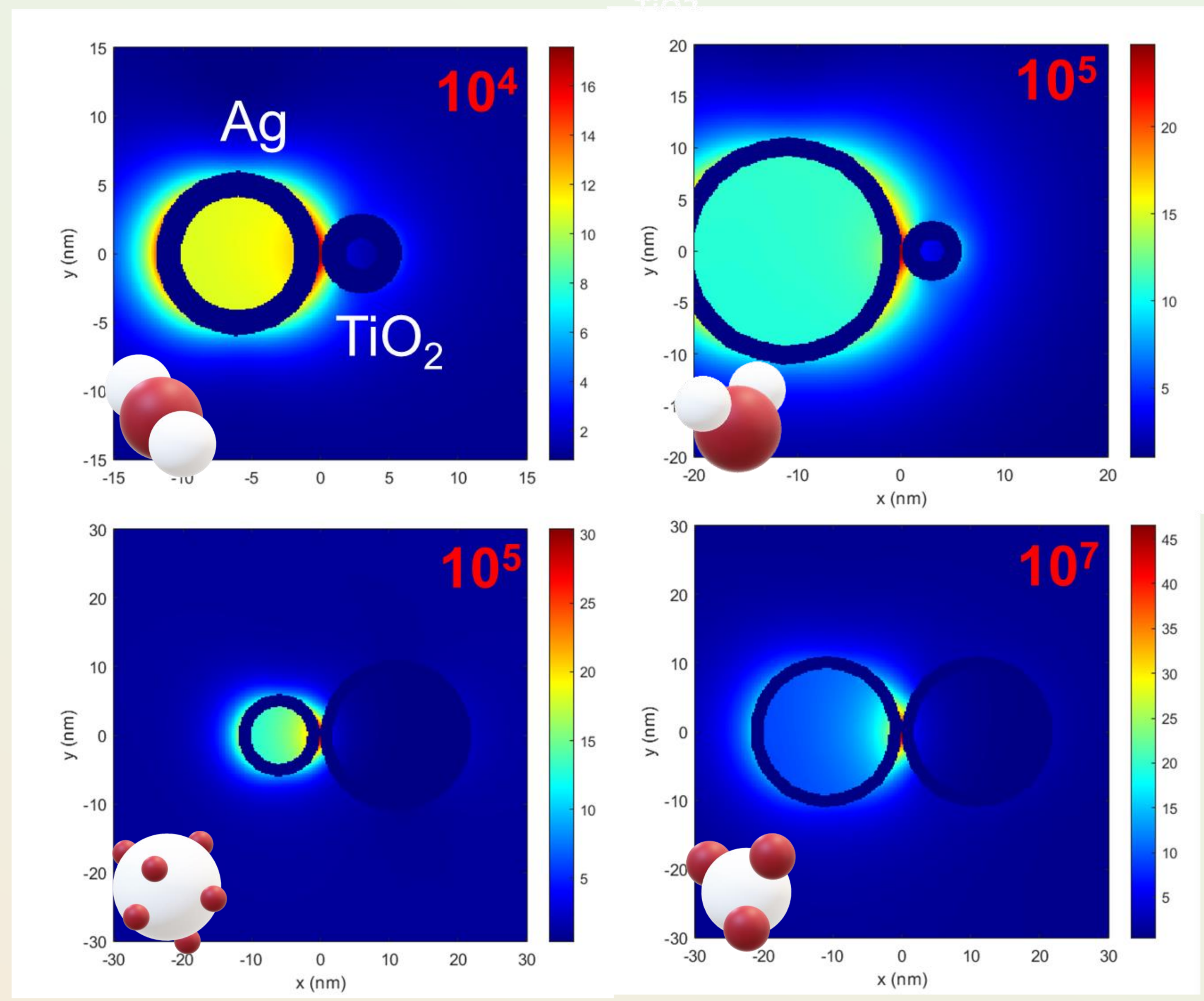
Conduction band shift (~0.14V) induced by Ag/TiOx/TiO_2 distorted interface.

LED (nm): — 365 — 405 — 455



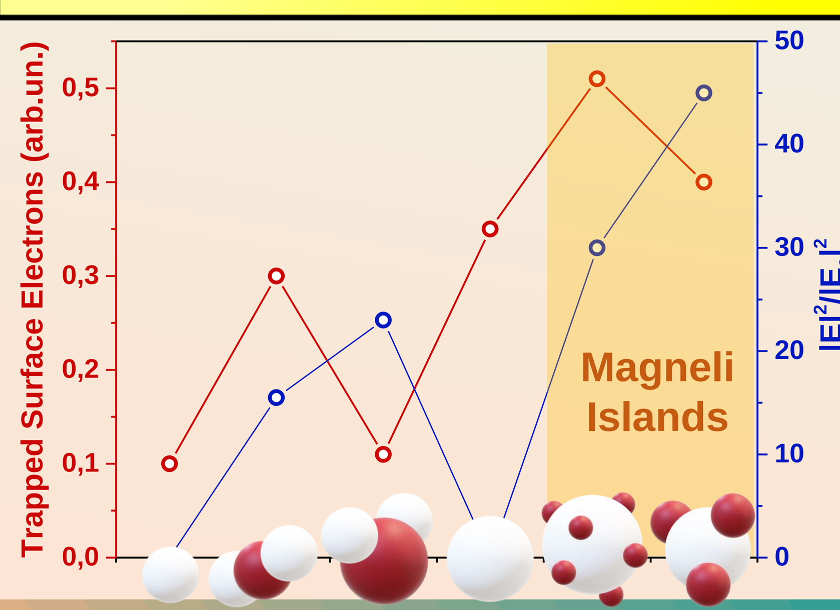
Under visible light, increased Ag content promotes localized electrons in TiO_2 surface, thus amplifies electron trapping. Therefore, Magneli islands increases the population of Ti^{3+} sites in Ag/TiO_2 interface, that facilitate carrier separation.

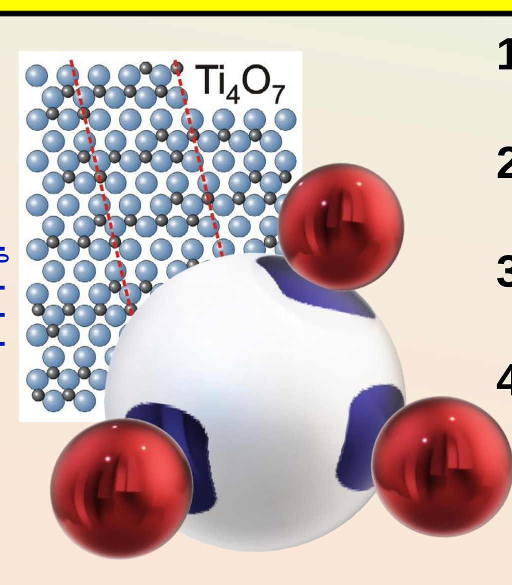
INTERFACIAL HOT SPOTS



During formation in flames, Ag/TiO_2 contact can be approximated as an ideal dimer. The flame acts as a light source that stimulates LSPR on Ag during formation and deposition on TiO_2.
The concentrated light in nano-proximity arises the enhanced local electric fields in particle's surface, known as hot spots. Hot spots promote the TiO_2 surface reduction by the hydrocarbons in the flame, thus the formation of Magneli nano-islands.

CONCLUSIONS





1. One step synthesis of visible-active "black" Ag/TiOx/TiO_2 using flame spray pyrolysis.
2. Plasmon-driven formation of Magneli islands in Ag/TiO_2 interface.
3. Hot spots promote the surface reduction and Ti^{3+} sites by combustion intermediates.
4. Controlling both components' particle size reveals the plasmon-induced hot electron dynamics and hot spot distribution.

REFERENCES

[1] K. Fujiwara, Y. Deligiannakis, C. G. Skoutelis, S. E. Pratsinis, Applied Catalysis B: Environmental 2014, 154–155, 9–15.
[2] M. L. Brongersma, N. J. Halas, P. Nordlander, Nature Nanotechnology 2015, 10, 25–34.
[3] E. Cortés, Science 2018, 362, 28–29.
[4] E. Cortés, W. Xie, J. Cambiasso, A. S. Jermyn, R. Sundararaman, P. Narang, S. Schlücker, S. A. Maier, Nature Communications 2017, 8, 14880.
[5] G. Liu, Y. Lou, Y. Zhao, C. Burda, Acc. Chem. Res. 2022, 55, 1845–1856.

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