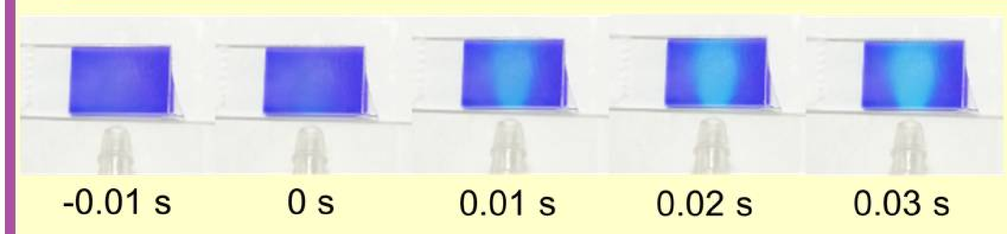
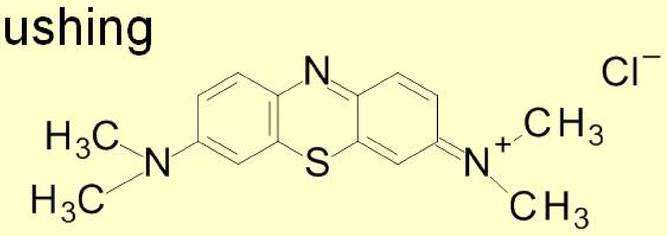
Quantitative analysis of water for understanding electron injection processes in dye-sensitized nanocrystalline semiconductor films

Ryota Ishizaki, Ryuzi Katoh *(Nihon Univ.)*

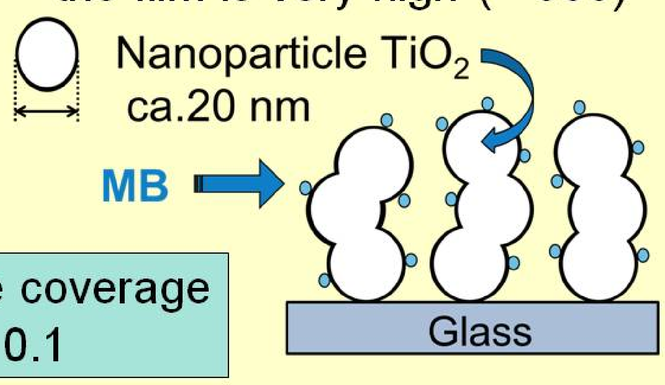
Fast-response Humidity-sensing Films based on Methylene Blue(MB)



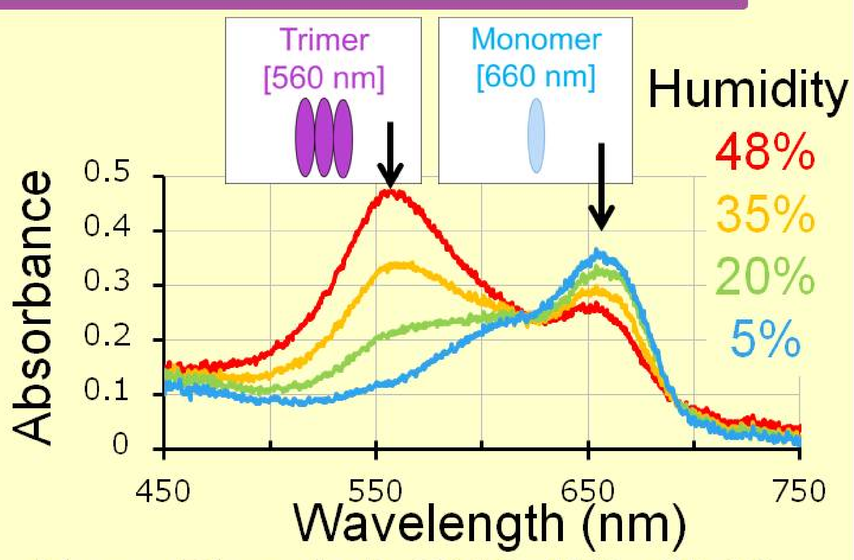
Color change of MB/TiO_2 by dry argon gas flushing



Specific surface area of the film is very high (~ 500)



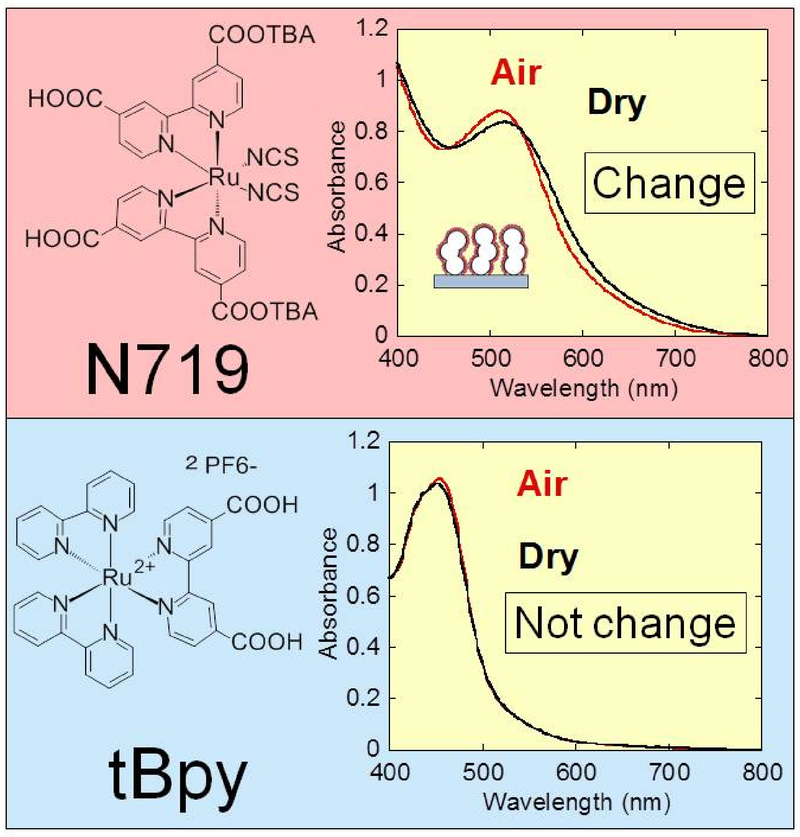
Dye coverage
θ = 0.1



R. Ishizaki, R. Katoh, *Chem. Phys. Lett*, 2016, 652, 36-39.

Vapochromism

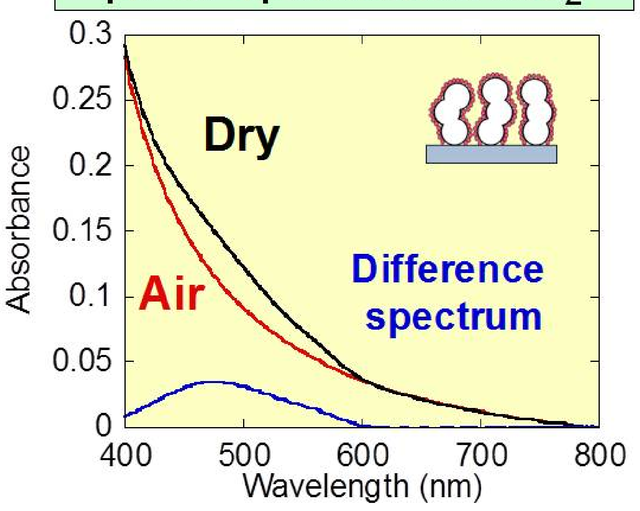
Absorption spectra of Dye/TiO_2



Color change may be due to solvent effect surrounding SCN group

Surface pH

Absorption spectra of phenolphthalein/TiO_2

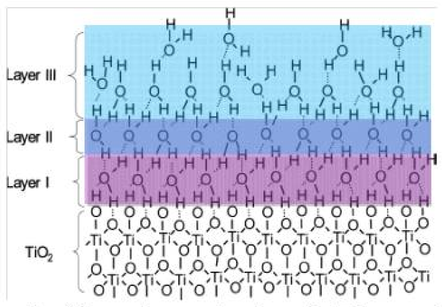


RH=50%	RH=0%
Colorless	490 nm
pH 0~8.2	pH<0

[H^+] around dye molecule increases dramatically by drying

Surface water

Adsorbed water on TiO_2 surface

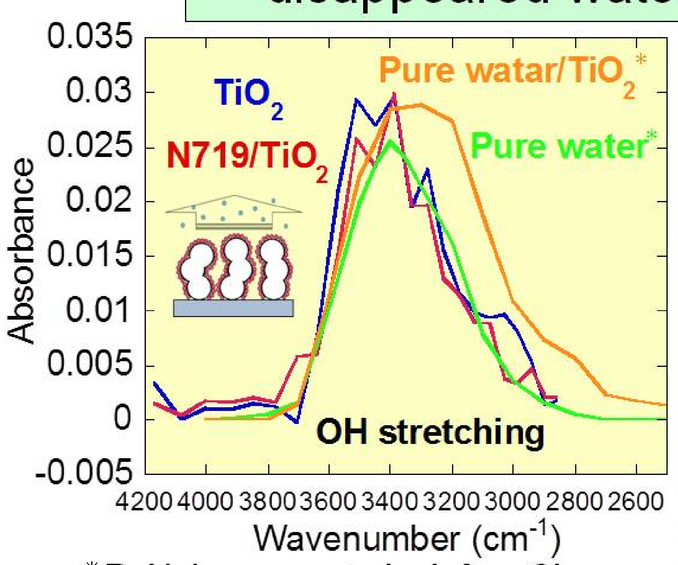


・Loosely physisorption

・Tightly bound chemisorption

A. Nosaka, et al., *J. Phys. Chem. B* 108 (2004) 9121-9125.

IR Absorption spectra of disappeared water by drying



・0.1~0.2 layer of water disappears

・Amount of lost water is not affected by the presence of dye on the surface

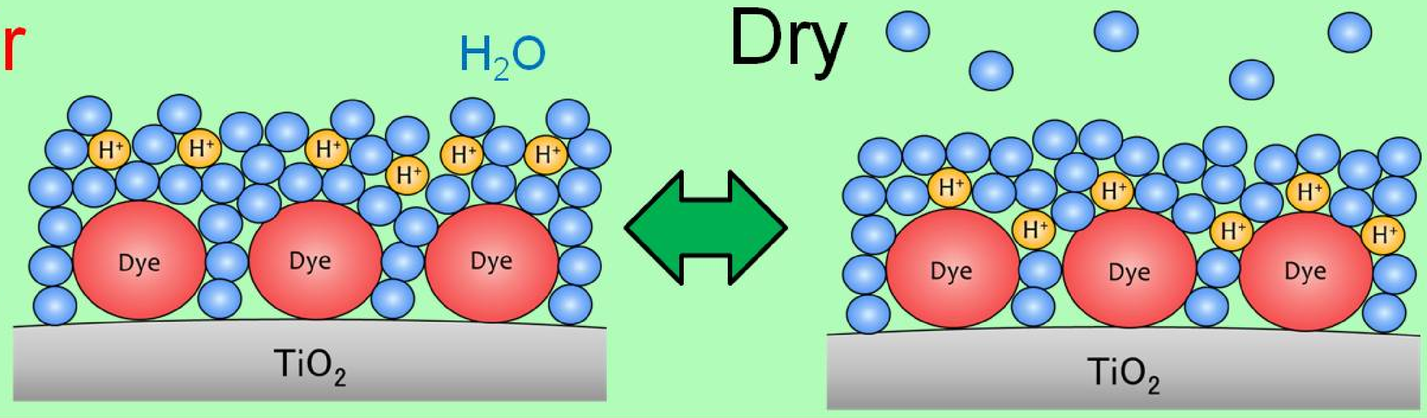
・Lost water molecules were adsorbed on TiO_2 physically

* R. Nakamura, et al., J. Am. Chem. Soc., 2003, 125, 7443–7450.

Model

・H^+ is located on the surface region

・Adsorbed dye molecules are immersed in the water layer

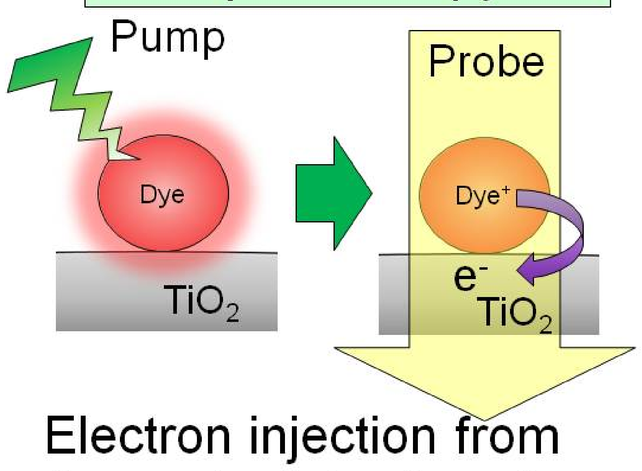


・0.1~0.2 layers of water disappears by drying

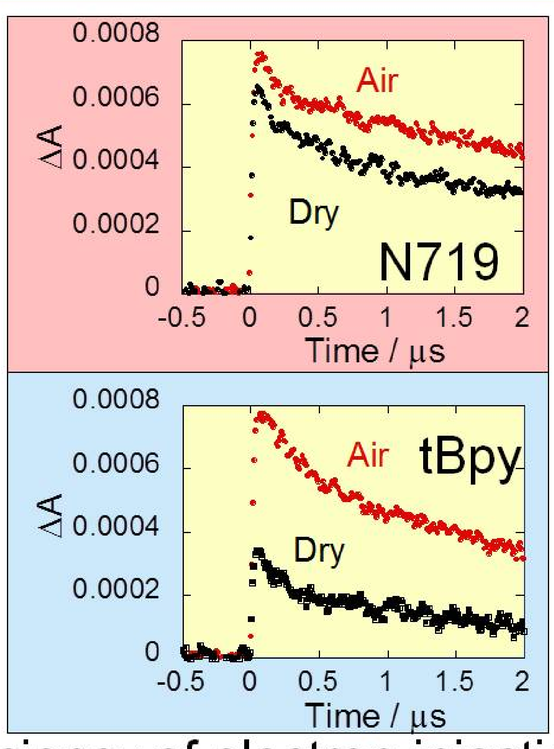
・[H^+] surrounding dye increases dramatically

Electron injection

Transient Absorption Spectroscopy

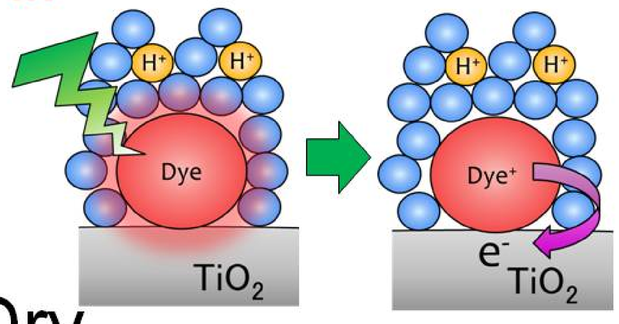


Electron injection from the excited dye into the TiO_2 particle

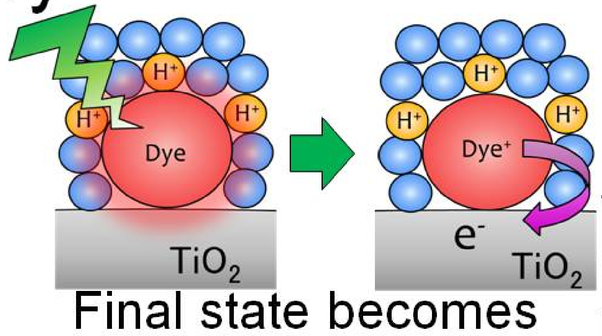


Efficiency of electron injection was reduced by drying

Air Initial state Final state

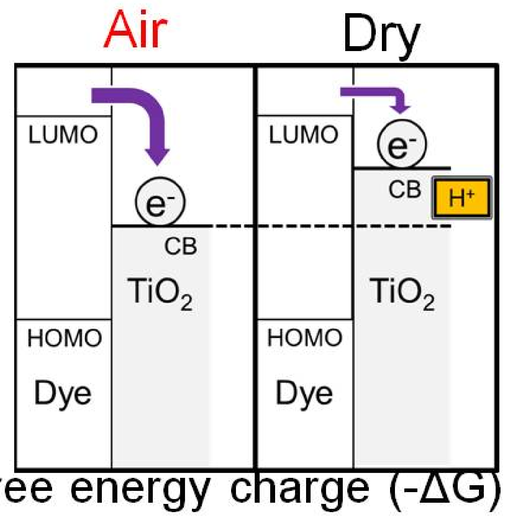


Dry



Final state becomes unstable due to H^+

Energy diagram



Free energy charge (-ΔG) for electron injection is effectively reduced by the presence of H^+ surrounding dye molecules