

Radiolysis of Water Confined in Aluminosilicate Nanotubes: Importance of Charge Separation Effects

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Imogolite nanotubes are interesting and highly-curved natural clay minerals described as having a wall polarization allowing them to separate photo-generated charge carriers. They can also be used as nanoreactors. These systems are therefore appealing to study confined water properties [1], charge separation effects [2] and how water radiolysis can be affected in these 2D-nanoscale environments [3].

Two types of aluminosilicate nanotubes were synthesized and studied: one is hydrophilic on its external and internal surfaces (IMO-OH), while the other has a hydrophobic internal cavity due to Si-CH₃ bonds (IMO-CH₃), the outer surface remaining hydrophilic. Picosecond pulsed radiolysis experiments have demonstrated that electrons are efficiently transferred outside the nanotubes. Coupled to gas production measurements as a function of the water content, these experiments have evidenced that, for imogolite samples containing very few water molecules on the outer surfaces (about 1% of the total mass), quasi-free electrons are formed. They attach to a water molecule, generating a radical water anion, which ultimately leads to the formation of dihydrogen. When more external water molecules are present, solvated electrons, precursors to dihydrogen, are formed.

The attachment of the quasi-free electron to water is a very efficient process, which accounts for the high production of dihydrogen for low values of relative humidity. When the water content increases, the solvation of electrons is predominant compared to the attachment to water molecules. Solvation of electrons therefore leads to the production of dihydrogen, although to a lower extent than when the precursors are quasi-free electrons.

On the other hand, the holes move towards the inner surface of the tubes. They mainly lead to the formation of dihydrogen and methane in irradiated IMO-CH₃.

Our radiolysis experiments therefore demonstrate the wall-induced spontaneous charge separation in these inorganic nanotubes, and stresses how these confined environments affect water radiolysis.

References:

[1] Liao, Picot, Lainé, Brubach, Roy, Thill & Le Caër (2018), *Nano Research* 11, 4759-4773.

[2] Pignié, Patra, Huart, Milosavljević, Renault, Leroy, Nicolas, Sublemontier, Le Caër & Thill (2021), *Nanoscale* 13, 19650-119662.

[3] Pignié, Shcherbakov, Charpentier, Moskura, Carteret, Denisov, Mostafavi, Thill & Le Caër (2021), *Nanoscale* 13, 3092-3105.