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Imogolite nanotubes are potentially promising co-photocatalysts because they are predicted to have curvature-induced, efficient electron-hole pair separation. This prediction has however not yet been experimentally proven. Here, we investigated the behavior upon irradiation of these inorganic nanotubes as a function of their water content to understand the fate of the generated electrons and holes.[1] Two types of aluminosilicate nanotubes were studied: one is hydrophilic on its external and internal surfaces (IMO-OH) and the other has a hydrophobic internal cavity due to Si-CH_3 bonds (IMO-CH_3), with the external surface remaining hydrophilic (AlOH groups). The pre-requisite to such a study is a detailed understanding of the structure and dynamics of water in these nanotubes. Analysis of the O–H stretching band as a function of the relative humidity (RH) provided information on the H bonding of confined water molecules.[2] Adsorption begins in the IMO-OH tubes at the lowest RH (< 10%). The inner surface of the tubes is first covered with water molecules; then, the central part of the tubes is filled, leading to very strong H-bonds. In contrast, the H bonds of water adsorbed on the outer surfaces of these tubes are weaker. Water dynamics in IMO-OH was also revealed by quasi-elastic neutron scattering experiments.[3] When one water monolayer is present on the inner surface, water molecules can jump between neighboring Si-OH sites. When IMO-OH is filled with water, the H-bond network is very rigid, and water molecules are immobile on the timescale of the experiment. A different scenario is observed for water inside IMO-CH_3. Weakly H-bonded water molecules are present. Water confinement in imogolites is then governed by the hydrophilicity of the inner walls. Upon irradiation, picosecond pulse radiolysis experiments demonstrated that the electrons are efficiently driven outward.[1] For imogolite samples with very few external water molecules, quasi-free electrons are formed. They are able to attach to a water molecule, which ultimately leads to dihydrogen. When more external water molecules are present, solvated electrons, precursors of dihydrogen, are formed. In contrast, holes move towards the internal surface. The attachment of the quasi-free electron to water is a very efficient process and accounts for the high dihydrogen production at low RH values. Our experiments demonstrate the spontaneous curvature-induced charge separation in these inorganic nanotubes.

References

[1] "Confined water radiolysis in aluminosilicate nanotubes: the importance of charge separation effects", M.-C. Pignié, V. Shcherbakov, T. Charpentier, M. Moskura, C. Carteret, S. Denisov, M. Mostafavi, A. Thill, S. Le Caër, *Nanoscale*, 13, 3092 (**2021**).

[2] "Tuning the properties of confined water in standard and hybrid nanotubes: An infrared spectroscopic study", Y. Liao, P. Picot, M. Lainé, J.-B. Brubach, P. Roy, A. Thill, S. Le Caër, *Nano Research*, 11, 4759 (**2018**).

[3] "Dynamics in hydrated inorganic nanotubes studied by neutron scattering: towards nanoreactors in water", S. Le Caër, M.-C. Pignié, Q. Berrod, V. Grzimek, M. Russina, C. Carteret, A. Thill, J.-M. Zanotti, J. Teixeira, *Nanoscale Adv.*, 3, 789 (**2021**).