Mapping hydration water structure and dynamics by Overhauser DNP relaxometry

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What are the key surface metrics that control interfacial water dynamics, and thus what are the associated "rules" for programming surfaces to tune their properties? In order to answer these questions, we need to measure the operational surface hydrophilicity and hydration barrier. These are difficult to access metrics, especially on soft material and biomolecular surfaces, and hence are not established. My group introduced equilibrium, single particle, surface water diffusivity as empirical measures of surface hydrophilicity that can be conceptualized as a molecular level "contact angle". Such measurements are enabled by a nuclear magnetic resonance (NMR) relaxometry technique termed Overhauser dynamic nuclear polarization (ODNP) that is sensitive to the diffusivity of water within 1 nm of surfaces, marked by site-specific nitroxide radical spin labels. I will present our ODNP study of amorphous silica surfaces with systematically varying silanol coverage [1], globular protein surfaces with site-specific spin labels [2], and of polymer surfaces with systematically varying hydrophilicity and hydrophobicity, achieved by varying the surface chemistry patterns. The results show how essential it is to consider the impact of heterogeneities in surface chemistry and their spatial patterning on the hydration water structure and dynamics. The significance of understanding the surface programing of hydration water structure and dynamics is that this is expected to reflect on the hydration barrier that tune adsorption and transport properties near the hydrated surfaces. NMR relaxometry, especially in the form of ODNP, is turning out to be a key technique contributing to this important topic.

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2. R. Barnes, S. Sun, Y. Fichou, F.W. Dahlquist, M. Heyden, S. Han, Spacially Heterogeneous Surface Water Diffusivity around Structured Protein Surfaces at Equilibrium, J. Am. Chem. Soc., 139 (49) (2017) 17890-17901.