Exploring Nanocrystal Interfaces using Magic Angle Spinning Dynamic Nuclear Polarization

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The combination of magic angle spinning and high-field dynamic nuclear polarization (MAS-DNP) [1] has revolutionized **solid-state NMR spectroscopy for surface science** [2]. Surfaces and interfaces can be crucial to a material's properties and applications, although they usually make up only a small fraction of the studied system. Hence, the sensitivity gains achieved with MAS-DNP can be required to permit detailed selective NMR analyses of surface/interface environments.

Sensitivity is a key limitation especially when the low relative abundance of interfacial nuclei is combined with unfavorable NMR properties, such as low receptivity (low natural isotopic abundance of stable, NMR-active isotopes and/or small gyromagnetic ratio). This is the particular case for the highly-unreceptive nucleus, calcium-43 (natural abundance ~0.14 %). **Calcium is a key element in many natural and synthetic materials**. It is the 5th most abundant element in the Earth's crust as well as in the human body, where it is present in **bones and teeth** in the form of substituted **hydroxyapatite**. Here, it will be shown that MAS-DNP is not only extremely pertinent for **detecting poorly-receptive ^{43}Ca at natural isotopic abundance in synthetic substituted hydroxyapatite nanocrystals** (NCs) **and mice teeth**, but it provides enough NMR sensitivity to be able to record 2D correlation spectra, allowing the distinction of **surface** and **core** calcium environments (see **Figure 1**) [3]. This selective insight is crucial to the understanding of how organic molecules interact with the mineral component of bone, which will help shed light on bone degeneration such as osteoporosis.

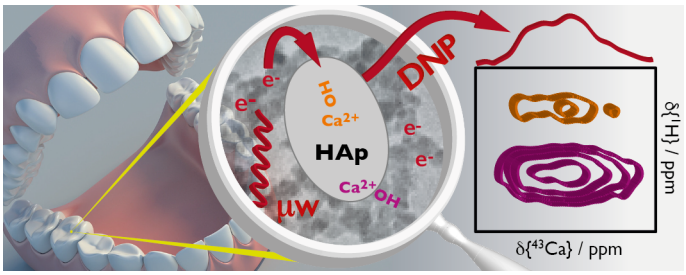

Figure 1. MAS-DNP allows distinguishing core (orange) from surface (purple) natural ^{43}Ca in hydroxyapatite.

Interfacial interactions are also extremely important in ligand-stabilized NCs. In particular, **zinc oxide** (ZnO) NCs are of large interest due to their versatility and **unique catalytic and electro-optical characteristics**, which are dependent on the character of the resulting nanocrystal-ligand interface including the ligand dynamics, their packing density, and their binding mode and/or affinity. Although the bulk structure of many NCs can be determined accurately by numerous methods including microscopic techniques and crystallography, the unambiguous characterization of these critical interfaces is still challenging. Here, it will be shown that with MAS-DNP providing the necessary sensitivity, **multiple 2D homonuclear NMR correlation spectra** can be recorded and **can be used to help extract unprecedented information concerning ligand arrangements on NC surfaces**, notably providing coordination modes and inter-ligand distances. This analysis unveils the vast difference between the organic-inorganic interfaces resulting from two synthetic routes to ZnO NCs: a traditional **sol-gel approach** and a recent One-pot Self-Supporting OrganoMetallic (**OSSOM**) procedure that uses organophosphorous compounds as capping ligands (see **Figure 2**) [4]. MAS-DNP-enhanced NMR not only supplies a detailed NC surface analysis but also demonstrates the superiority of the OSSOM approach for the preparation of high quality quantum-sized ZnO crystals.

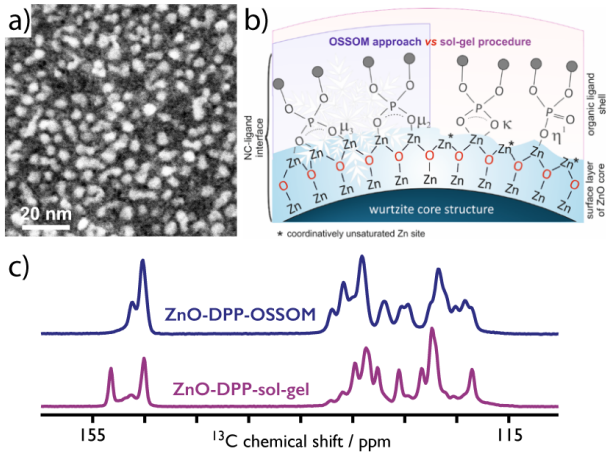

Figure 2. Zinc oxide nanocrystals (STEM in (a)) with diphenylphosphate ligands (schematic in (b)) prepared using different synthetic procedures display contrasting organic-inorganic interfaces (via ^{13}C NMR spectra (c)).

References

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