Zirconium and hafnium oxide nanocrystals and oxo clusters

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Colloidal nanocrystals are usually hybrid inorganic-organic objects. They have an inorganic, crystalline core which is capped by a layer of organic surfactants. Metal oxide nanocrystals find application in solar cells, batteries, bio-imaging, etc. On the other hand, oxo clusters are building blocks in metal organic Frameworks (MOFs) with exciting catalytic properties.

First, we introduce surfactant-assisted synthesis of colloidal nanocrystals and the (undesired) chemistry that can occur with solvents and ligands.[1] Second, we elaborate on the precursor chemistry during the synthesis of zirconium and hafnium oxide nanocrystals.[2] After establishing an E1 elimination mechanism, we focus on the crystallization mechanism and find that an amorphous phase precedes the crystalline nanoparticles. Third, we develop a comprehensive picture of the surface chemistry of these metal oxide nanocrystals. We establish ligand exchange rules in both nonaqueous and aqueous media.[3] As such, we find the optimal binding moiety for physiological conditions; nitrodopamine derivatives. Tailoring the surface chemistry allows to use hafnium oxide nanocrystals as contrast agent in Computed Tomography (CT) imaging. We will discuss both in vivo and ex vivo applications of such contrast agents. Finally, we take the oxo clusters out of the MOF and consider it an atomically precise nanocrystal. Using the same ligands as for nanocrystals, the clusters are endowed with the same solubility properties and become useful catalysts.[4] The cluster-catalyzed reaction has a five times higher rate than the nanocrystal-catalyzed reaction. To analyze the soluble clusters, we use X-ray total scattering and Pair Distribution Function analysis.

We thus present here a comprehensive overview of oxide nanochemistry, focusing on group 4 metals.
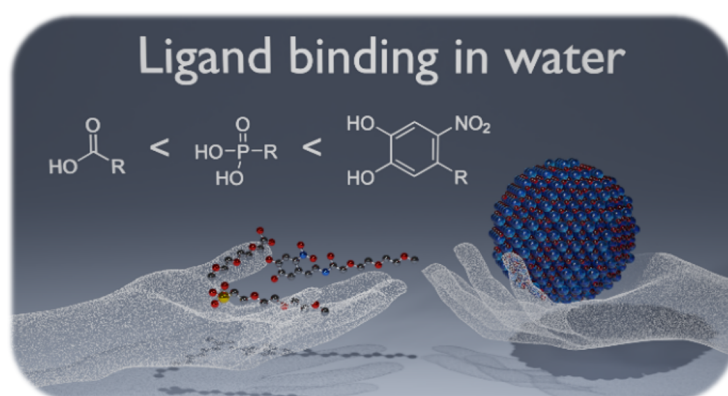
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