Mechanistic Studies on Metal Aerogels and their Application in Electrocatalysis

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Some ten years ago we fabricated the first aerogels based on metal nanoparticles.[1] The gels are formed either via preformed colloidal nanocrystals (two step approach) or directly from the respective metal salt solutions (one step approach). Both synthetic procedures yield similar structures as gels and as aerogels providing finely interconnected three-dimensional metal meshes displaying densities of about 1000th of the respective bulk materials. Currently, the materials space covers eight noble metals, a number of less noble metals and a multitude of mixtures of those (two, three or more components) with tuneable compositions.[2] While those materials find interest in various fields of applications (so far predominantly in (electro)-catalysis (see below) and sensing) the mechanisms of their aggregation and structure formation are still barely understood. In this presentation we will first touch upon theoretical considerations which will conclude in the operational function of diffusion-limited cluster aggregation with a certain contribution of diffusional rotation.[3] From the experimental side we will report on the effects specific ions play in the aggregation of Gold nanoparticles, we will elucidate the various roles a single chemical may play, namely as reducing agent, stabilizing ligand and salt with its influence on the ionic strength, and we will tell about the recently observed self-healing of metal gels.[4]

The work on the electrocatalysis on (multi-)metallic (aero-)gels [5] laid the foundation of the amelioration of the building blocks as a plausible approach to graft aerogels with distinguished properties while preserving the aerogel superiority. We report on the first case of an aerogel electrocatalyst composed entirely of alloyed PdNi hollow nanospheres with controllable chemical composition and shell thickness. This work expands the exploitation approach of electrocatalytic properties of aerogels into morphology and composition control of its building blocks.[6] In a further study, we prepared and analyzed a new class of hierarchical aerogels composed of multimetallic Ni-Pd_xPt_y nanoparticle building blocks with continuously engineered shape and compositions. This approach results in aerogels with hierarchical structures organizing the nanoscale regulated architecture and macroscale three-dimensional network structure.[7] As another example we`ll line out how core-shell structuring of pure metallic aerogels can be tuned towards highly efficient Pt utilization for the oxygen reduction reaction.[8] We will report on the first functioning polymer electrolyte fuel cell based on a metal aerogel catalyst [9] and most recent applications of noble metal aerogels in the hydrogen evolution reaction.[10] For gaining highest performance of these catalysts the surface chemistry [11] as well as the formation mechanisms have to be studied and tuned.[12]

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