A New Approach to Semiconducting Metal Chalcogenide Aerogel Formation via Electrogelation: Opportunities and Challenges

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Metal chalcogenide aerogels comprising an integrated semiconducting matter-pore network exhibit quantum confined optoelectronic effects characteristic of nanocrystals (quantum dots) with a large, interfacial surface area for interaction with the ambient. As such, they have unique advantages for applications involving photo- and/or electrochemical sensing and catalysis, providing the material can be appropriately integrated into a suitable device architecture. Traditional synthesis of chalcogenide aerogels involves (1) the synthesis of metal chalcogenide quantum dots; (2) ligand capping with thiolate "protecting groups" bound to surface metal ions, (3) deprotection with a chemical oxidant to form molecular disulfides plus loss of surface metal ions to expose chalcogenide ions, and (4) oxidative assembly of particles via interparticle di-chalcogenide bond formation. This approach is robust for a wide range of chalcogenides, and produces free-standing gels and aerogels. As a means to interface chalcogenide aerogels to device structures, we considered whether gelation could be achieved by electrochemical oxidation. In the presentation, the successful application of electrochemical gelation approaches to a range of metal chalcogenides (CdS, CdSe, ZnS) will be described and the mechanism of formation will be discussed in the context of similarities and differences to chemically prepared chalcogenide aerogels. We will conclude with a discussion of the opportunities and challenges for the exploitation of this methodology to produce electrochemical sensors and catalysts.