Tiny gaps between metals enable extreme field enhancements and strongly modified light-matter interactions promising for ultrafast optoelectronics, energy applications and on-chip components for quantum information processing. We use creative nanofabrication techniques at the interface between chemistry and physics to realize nanostructures with critical dimensions on the atomic- and molecular-scale (1-10 nm), together with advanced, ultrafast optical techniques to probe the emerging phenomena. Here, I will provide an overview of our recent research demonstrating tailored light-matter interactions by leveraging ultra-small plasmonic cavities fabricated with bottom-up techniques. Examples of our demonstrations include 1,000-fold Purcell enhancements [Nature Photonics 8, 835 (2014)], ultrafast single photon sources [Nano Letters 16, 270 (2016)], tailored emission from two-dimensional semiconductor materials [Nano Letters 15, 3578 (2015), ACS Photonics 5, 552 (2018)], perfect absorbers and combinatorial plasmonic colors [Advanced Materials 27, 7897 (2015), Advanced Materials 29, 1602971 (2017)].