

## Synthesis and Applications of Confined Plasmonic Nanoparticles in Hollow Structures

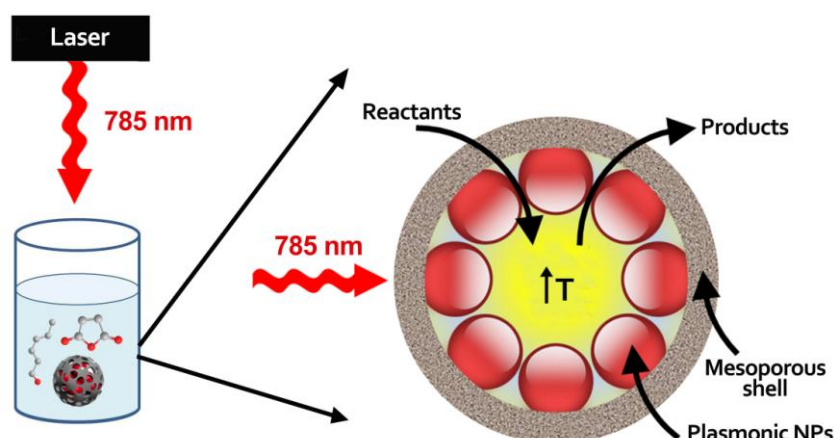
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### Abstract

The synthetic architectures of complex nanostructures, including multifunctional hollow capsules, are expected to play key roles in many different applications, such as drug delivery, photonic crystals, nanoreactors, and sensing. Implementation of novel strategies for the fabrication of such materials is needed because of the infancy of this knowledge, which still limits progress in certain areas. We report herein the design of plasmonic hollow nanoreactors capable of concentrating light at the nanometer scale for the simultaneous performance and optical monitoring of thermal-activated reactions. These reactors feature the encapsulation of plasmonic nanoparticles on the inner walls of a mesoporous silica capsule. A Diels-Alder cycloaddition reaction was carried out in the inner cavities of these nanoreactors to evidence their efficacy. Thus, it is demonstrated that reactions can be accomplished in a confined volume without alteration of the temperature of the bulk solvent while allowing a real time monitoring of the reaction progress. Additionally, these plasmonic nanoprobe have been shown as an advanced intracellular hybrid SERS sensor for relevant signaling molecules (NO). After their inner functionalization with a NO chemoreceptor, the sensor is quantitative and can perform in-situ, real-time monitoring of the dynamics of intracellular NO in living cells while remains fully biocompatible. Its sophisticated design prevents the interaction of cytosolic macromolecules within the active optical material and the enzymatic degradation of the sensor. It additionally facilitates the diffusion of small molecules between the interior and exterior thanks to the plasmonic thermal gradients generated upon their illumination.



**Figure 1.** Schematic cross-section view of the plasmonic nanoreactors developed in this work where reactants and products diffuse through the mesoporous silica shell and a NIR-laser irradiation promotes the chemical reaction allowing a simultaneous in situ SERS monitoring of the process.