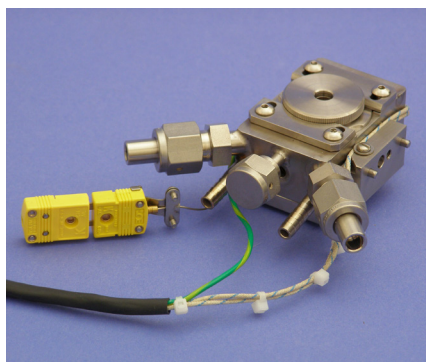


# Microscale Silica "Lens" for Plasmonic CO<sub>2</sub> Hydrogenation in the Harrick Scientific Raman Reaction Chamber

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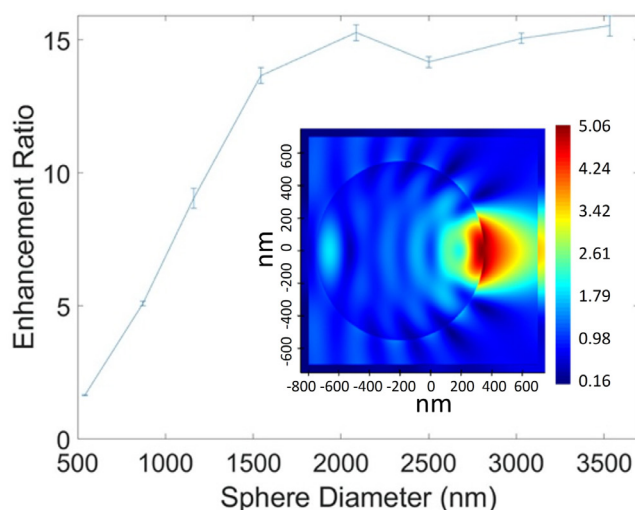


Harrick Scientific's Raman Reaction Chamber (HVC-MRA-5).

Figure 1. Inset: Lumerical simulation of a 1.1  $\mu\text{m}$  silica nanosphere under 532 nm illumination. Plot: Raman enhancement due to the silica sphere

## INTRODUCTION

Plasmonic nanoparticle catalysts are uniquely able to generate and transfer photoexcited carriers at high temperatures for efficient harnessing of solar energy to drive chemical reactions. Studies have found a linear relationship between reaction rate and light intensity<sup>1</sup>. We aimed to leverage this super linear relationship for the case of CO<sub>2</sub> hydrogenation over rhodium nanoparticles supported on TiO<sub>2</sub> by focusing light on the nanoscale as focusing light with a macroscopic lens would create a single large spot, creating an extreme thermal gradient across the catalyst surface. An optimal temperature and intensity exists since higher temperatures can kinetically increase reaction rates, while physically hindering hot carrier generation of the nanoparticle catalyst. Thus, it was hypothesized that lens or a series of lenses which could focus the light onto many different points on the catalysts surface would enable thermal transfer between the hot focal points and neighboring area, which would prevent the focal points from overheating to maintain a relatively constant surface temperature. To do so, silica



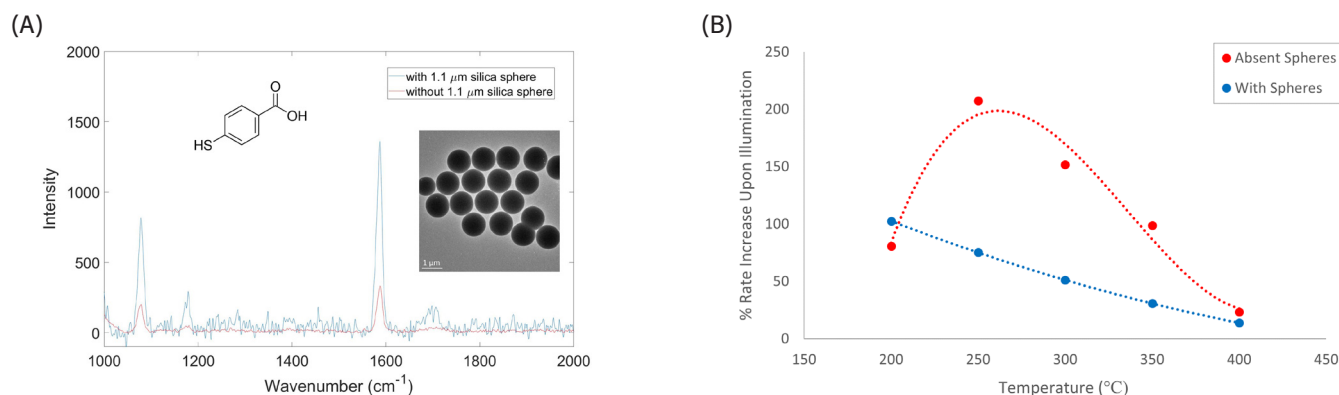


Figure 2. (A) Raman spectra of pMBA with characteristic peaks at  $\sim 1080$  and  $1580\text{ cm}^{-1}$ . Inset shows TEM image of silica nanosphere (B) Decrease in relative light enhancement upon illumination. Dotted line is a fitted polynomial trend.

nanospheres were synthesized and their nanophotonic character simulated and evaluated using Raman spectroscopy. Finally, the silica spheres were added to a plasmonic Rh/TiO<sub>2</sub> catalyst and the performance compared for CO<sub>2</sub> hydrogenation reaction. Using a Thermo Fisher Scientific DXR2 Raman microscope with the Harrick Raman Reaction chamber (HVC-MRA-5) heated with the Harrick Temperature controller (ATK-024-3) enabled this investigation.

## METHODS

Nanoscale spherical lens were synthesized following a Stöber seeded growth method<sup>2</sup>. Rhodium nanoparticles were synthesized using a polyol reduction method<sup>3</sup>. Rhodium (III) Chloride was reduced by ethylene glycol at 160 °C in the presence of PVP. The nanoparticles were washed, diluted, and incorporated onto TiO<sub>2</sub> support by wet impregnation method<sup>3</sup>. The dried catalyst was finely ground a mortar pestle and calcinated in air for 3 hours at 400 °C. Before each reaction the catalyst is reduced in the Harrick Raman Reaction chamber (HVC-MRA-5) using hydrogen. Au nanoparticles were synthesized using the Turkevich method<sup>4</sup>.

## RESULTS AND DISCUSSION

Nanophotonic character of silica nanospheres was simulated using Lumerical's FDTD software. As

sphere diameter increased, the light concentrated is increasingly focused rearward as the particle diameter becomes significantly larger than the incident wavelength. The simulation indicated that the electric field of light would be 5x stronger immediately opposite the illuminated side (Figure 1. Inset). The simulation was confirmed using Raman spectroscopy of a silicon wafer also taken at 532 nm illumination. As the sphere diameter increased, the Raman signal also increased until it plateaued at  $\sim 15$ x fold enhancement from a 1500 nm sphere. This was consistent with a prior report<sup>5</sup>. To test whether this enhancement would be compatible with the plasmonic enhancing of noble metal nanoparticles, a Raman reporter pMBA was added to a gold nanoparticle monolayer and the silica sphere was placed atop the functionalized nanoparticle monolayer. As seen in Figure 2, the enhancement of the plasmonic nanoparticle was further increased by the addition of a 1.1 μm silica sphere (Figure 2 Inset). However, this demonstrated enhancement did not translate to the plasmonic photochemical reaction rate. No suitable way to add the nanoscale lens to the catalyst bed was found. Adding in solution wetted the catalyst which compacted, creating mass transport issues and the spheres did not form an even layer. When added dry, no method was found to evenly distribute them in a monolayer over the catalyst.

## CONCLUSION

Silica nanospheres were synthesized and the nanophotonic behavior evaluated via Raman spectroscopy. The enhancement confirmed the behavior simulated using Lumericals FDTD solver. A Rh/TiO<sub>2</sub> catalyst for plasmonic CO<sub>2</sub> hydrogenation was synthesized and performed as expected on its own. But ultimately, no method was found to place the silica spheres as a uniform monolayer onto the catalyst to combine the enhancement of the plasmonic nanoparticles with the enhancement of the silica sphere. To avoid this issue in the future, optically tailored supporting particles should be integrated into the catalyst itself and not added after the fact, which will be explored.

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