

## Objectives

The primary goal of the proposed research is to demonstrate the synthesis of catalytically active nanostructured metal-oxide composites using PLASMER. This simultaneous laser ablation and reduction approach has the potential to rapidly form diverse metal-oxide composite materials. The research objectives are:

1. Synthesis of two classes of metal-oxide materials
  - a. Metal nanoclusters supported on oxide nanoparticles
  - b. Metal nanoparticles deposited onto nanostructured solid oxide surfaces
2. Assessment of the catalytic activity of the synthesized materials towards the reactions
  - a. Reduction of 4-nitrophenol with  $\text{NaBH}_4$
  - b. Thermochemical hydrogenation of  $\text{CO}_2$

We have nearly completed Objective 1 and made substantial progress on Objective 2 during this reporting period.

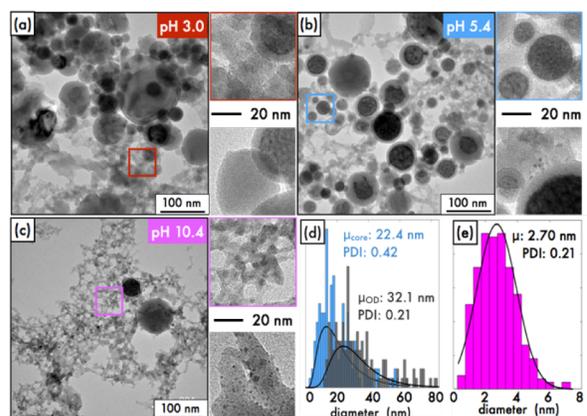
## Research Progress

### Objective 1a

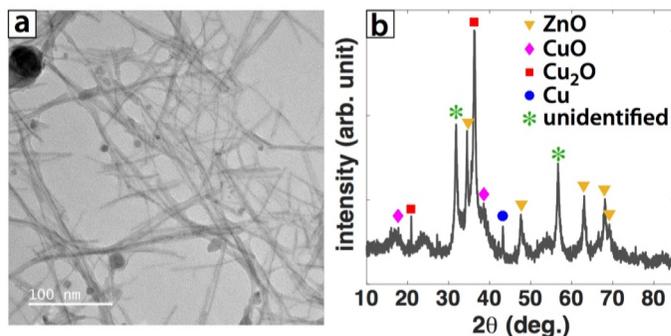
We have completed investigation of silica-Au nanocluster synthesis from PLASMER of aqueous tetrachloroaurate ion and a silicon wafer, with the results published in *Appl. Surf. Sci.* in January 2019. This synthesis yielded ultrasmall 2 nm Au clusters stabilized in an amorphous silica matrix, along with a side product of larger 7 nm Au nanoparticles that were not attached to silica and could be removed by centrifugation.

By replacing tetrachloroaurate with copper(II) nitrate, we synthesized silica-Cu composite materials with pH-dependent morphologies (Figure 1). While large spherical Cu@silica core-shell nanoparticles dominate at pH 3.0 and 5.4, an amorphous silica matrix containing 2.7 nm Cu clusters is formed at pH 10.4. The Cu loading in the material synthesized at pH 10.4 is 36 wt.%, more than 10 times higher than for the materials synthesized at lower pH. We obtained a similar result when replacing the silicon wafer with zinc foil to obtain ZnO-Cu composites: 30% wt. Cu was deposited at pH 12, while 14 wt.% was deposited at pH 5. TEM and XRD analysis of this material shows fiber structures with multiple crystalline phases (Figure 2), including unidentified peaks that may indicate Cu-Zn alloying. These results suggest that PLASMER under basic pH conditions could deposit large amounts of Cu on any support. We tentatively attribute this capability to a strong electrostatic absorption mechanism, wherein the high pH produces negatively charged reactive species from the ablated surface that bond with the Cu precursor cations, and plan to investigate this hypothesis further.

It is notable that PLASMER of aqueous copper(II) nitrate produces solely silica-Cu or ZnO-Cu composite products, while Au, Ag, and Pd precursors produce the undesired side-product of large metal nanoparticles that are not incorporated into the support. We attribute this behavior to the low reduction potential of Cu, which prevents direct laser-induced reduction of  $\text{Cu}^{2+}$  to nanoparticles in the absence of the protective silica or zinc oxide support. We recently reported on how hydroxyl radicals induce overgrowth of Au nanoparticles in *Phys. Chem. Chem. Phys.* and *J. Phys. Chem. B*, and ongoing investigations into hydroxyl radical effects on Ag and Cu indicate these metals



**Figure 1:** TEM images (a)-(c) and size distributions (d)-(e) of silica-Cu composite materials.



**Figure 2:** TEM image (a) and XRD spectrum (b) of Cu-ZnO composite material synthesized at pH 12.

rapidly back-oxidize in the laser environment when no support material or radical scavenger is present. These studies have led us to conclude that PLASMER is particularly effective at producing composite materials from non-noble metal precursors, making the technique promising for rapid fabrication of inexpensive composite materials that may be used for catalysis and other applications.

#### Objective 1b

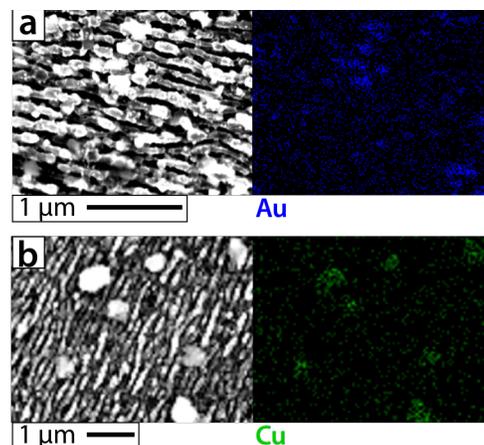
We have found that PLASMER enables the deposition of Au and Cu on to laser-induced periodic surface structures (LIPSS) formed upon ablation of a Si wafer in an aqueous tetrachloroaurate or copper(II) nitrate (Figure 3). The Au metal appears to be incorporated into the  $\sim 100$  nm LIPSS structures (Figure 3(a)), while the Cu forms isolated  $\sim 500$  nm particles on the LIPSS surface (Figure 3(b)). Preliminary XRD and XPS measurements of the Cu-Si surface suggest that these particles are made of the metastable phase copper silicide,  $\text{Cu}_3\text{Si}$ . As with the colloidal products described above, the loading of Au or Cu on the silicon LIPSS surface is strongly dependent on the initial solution pH, although the optimal pH is near neutral instead of basic. In the case of Au, 9 wt.% is deposited at pH 6.5, while only 3 wt.% is deposited at pH 3 or 12. Preliminary results suggest that pH near 7 is also optimal for Cu deposition, with up to 2.5 wt.% deposited as compared to less than 1 wt.% at pH 5 or 11. The distinct optimal solution pH ranges for metal deposition onto the solid Si surface as compared to ablated material in solution is unexpected and will be further investigated.

#### Objective 2

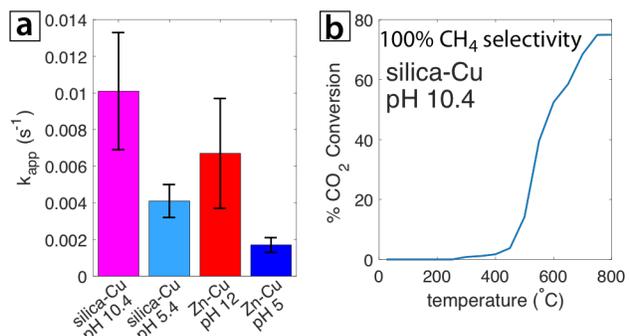
The colloidal silica-Cu and ZnO-Cu materials synthesized in Objective 1a are highly active towards the reduction of 4-nitrophenol with  $\text{NaBH}_4$ . On both supports, the catalysts synthesized at higher pH have exhibit a higher pseudo-first-order apparent rate constant  $k_{\text{app}}$ , consistent with higher Cu loading (Figure 4(a)). More importantly, we have obtained preliminary evidence that the silica-Cu material synthesized at pH 10.4 catalyzes thermochemical hydrogenation of  $\text{CO}_2$  with 100% selectivity towards methane (Figure 4(b)). The reaction was carried out under a constant flow of 10 mL/min Ar + 8 mL/min  $\text{H}_2$  + 2 mL/min  $\text{CO}_2$ . The reactor temperature was increased from 50 – 800 °C in 50 °C increments, with the gas mix after 1 hr of reaction at each temperature analyzed. Although the silica-Cu catalyst exhibits no appreciable  $\text{CO}_2$  hydrogenation activity until 400 °C, the 100% selectivity to  $\text{CH}_4$  is remarkable. Methane formation from  $\text{CO}_2$  is highly unusual for a Cu catalyst because most Cu-based catalysts in the literature produce predominantly CO and methanol. In the no-cost extension period, we will further investigate the  $\text{CO}_2$  reduction activity of this material and the Zn-Cu catalyst.

#### Research Impact

Four students (three graduate, one undergraduate) were directly supported by this funding. In addition, one undergraduate supported by an NSF-REU fellowship and one high school student supported by ACS Project SEED worked on the project in the summer. The students developed new protocols for laser synthesis and gained expertise in both materials characterization techniques and catalytic reaction operation. In addition to these laboratory skills, they also gained knowledge in data analysis, literature review, and scientific paper writing, which will prepare them for future STEM careers. The funding also allowed the PI to take one student to the Southeast Regional Meeting of the American Chemical Society (SERMACS) in November 2018 and a second student to the Laser Advanced Materials Processing (LAMP) conference in May 2019. Finally, this funding has allowed the PI to generate preliminary results for developing federal grant proposals. The PI is planning to submit a proposal on investigating PLASMER synthesis as a route to  $\text{CO}_2$  hydrogenation catalysts to the NSF this coming grant cycle.



**Figure 3:** SEM images (left) and EDX mapping (right) of (a) Au-Si and (b) Cu-Si LIPSS.



**Figure 4:** (a) Rate constant for nitrophenol reduction for four Cu-based catalysts. (b) Conversion of  $\text{CO}_2$  versus temperature for silica-Cu catalyst.