Title: Pulsed Laser Ablation Surface-Mediated Excitation and Reduction (PLASMER) as a One-Step Route to Nanostructured Metal-Oxide Composite Catalysts

PI: Dr. Katharine Moore Tibbetts, Department of Chemistry, Virginia Commonwealth University

Objectives
The primary goal of the proposed research is to demonstrate the synthesis of catalytically active nanostructured noble metal-oxide composites using PLASMER. This simultaneous laser ablation and reduction approach has the potential to rapidly form colloidal metal nanoparticles supported on metal oxides and metal nanoparticles deposited on nanostructured metal oxides. The research objectives are:

1. Synthesis of two classes of metal-oxide materials (metals: Au, Ag, Pd, Pt, Cu; oxides: Si, Ti, Zr, Zn, Al)
   a. Embedded metal nanoparticles (MNPs) in nanostructured oxide support
   b. Deposited MNPs on nanostructured oxide surfaces
2. Assessment of the catalytic activity of the synthesized materials towards the reactions
   a. Reduction of 4-nitrophenol with NaBH₄
   b. Oxidation of CO to CO₂

We have made progress on Objectives 1a, 1b, and 2a during the first year of this grant.

Research Progress

Objective 1a
PLASMER of aqueous KAuCl₄ with a Si target produces two types of silica-Au colloidal nanostructures shown in Figure 1(a): isolated 7.3±2.1 nm NPs that predominantly consist of Au (based on EDX) and 3.4±0.8 nm Au NPs embedded in an amorphous silica matrix. XPS analysis of the mixed product shows that multiple oxidation states of Au and Si are present (Figure 1(b)). These results have been submitted for publication to Appl. Surf. Sci.

We have also obtained preliminary data suggesting that PLASMER can produce bimetallic alloy AuAg and AuPd NPs embedded in silica in addition to pure Au and Ag NPs (Figure 2). UV-visible spectra (Figure 2(a)) of the PLASMER products of Si immersed in aqueous KAuCl₄, AgNO₃, a 1:1 mixture of KAuCl₄:AgNO₃, and a 1:1 mixture of KAuCl₄:Pd(NO₃)₂ show surface plasmon resonance (SPR) peaks consistent with metal alloying. The SPR peak of the silica-AuAg NPs lies directly in between the SPR peaks of the pure Au and Ag samples, and no visible Au SPR peak is present in the AuPd mixture. TEM analysis of silica-AuPd (Figure 2(b)) and silica-Ag (Figure 2(c)) also show the formation of large isolated NPs and smaller NPs embedded in the silica. In the absence of the Si target, Au and Pd NPs are readily formed from aqueous metal salt solutions with laser irradiation, which we expect leads to the formation of the large isolated NPs in the PLASMER experiments. However, Ag NPs were not formed in the absence of the Si target. We found that back-oxidation of Ag⁺ atoms by OH radicals formed in the laser plasma prevented Ag NP formation and that addition of a small amount of liquid ammonia as a radical scavenger leads to Ag NP formation. These results, published in Molecules, suggest that the Si target acts as a radical scavenger to enable formation of the silica-Ag NPs in Figure 2(c).

In the next year of the project, we plan to optimize the laser synthesis conditions to improve the NP size distributions in the PLASMER products. For instance, we will minimize the formation of the large ~20 nm silica-
Ag NPs visible in Figure 2(c) by adjusting the AgNO₃ concentration and laser parameters. We will also focus on optimizing the synthesis of bimetallic and trimetallic systems and will test other targets for oxide formation including Ti and Zr. Finally, we are developing centrifugation protocols for separating the isolated NPs from those embedded in the silica matrix in order to analyze the products separately.

Objective 1b

We have demonstrated that PLASMER enables the deposition of Au and Ag on to laser-induced periodic surface structures (LIPSS) formed upon ablation of a Si wafer in an aqueous 1:1 mixture of HAuCl₄ and AgNO₃. Figure 3(a) shows an SEM image of the Si-LIPSS with characteristic 100 nm period typical of LIPSS generated on an Si surface immersed in water using femtosecond laser pulses. Figure 3(b) shows the EDX analysis of a 500 x 400 µm area of the nanostructured surface, indicating the deposition of both Au and Ag. Because no obvious metal NPs are present on the LIPSS in Figure 3(a), we expect that the Au and Ag atoms are distributed on the surface either as isolated atoms or as clusters that are too small to resolve on the SEM image. Additional experiments using higher concentrations of HAuCl₄ show that the atomic percentage of Au deposited on the Si surface can be increased to ~2 wt%. In the next year of the project, we plan to further characterize these surfaces with X-ray techniques (XRD and XPS) to determine the phase structures of the surface species. We also intend to deposit metals including Pd and Cu on the Si surfaces with this technique.

Objective 2a

The colloidal silica-metal NPs synthesized in Objective 1a are highly active towards the reduction of 4-nitrophenol with NaBH₄. Figure 4 shows the catalytic rate constants for five PLASMER colloidal products. The AgAu and PdAu NPs were produced from a 1:1 mixture of the metal precursor salts. The rate constants kₘ are reported with respect to the amount of metal added to the reaction rather than to the available surface area, i.e. as s⁻¹ µmol⁻¹ instead of s⁻¹ L m⁻² as sometimes reported. Normalizing the rate constant with respect to the amount of added metal provides a means to directly assess how efficiently the metal atoms are used for the catalytic reaction, independent of the size dispersity of the nanocatalyst. The activity of the Si-Au NPs is slightly higher than several recently reported supported Au NP catalysts with kₘ values ranging from 0.03 to 0.09 s⁻¹ µmol⁻¹, and the ~3-fold higher activity obtained with the Si-AgAu NPs indicates that alloying the metals can further enhance the catalytic activity. In the next year of the project, we intend to assess the catalytic activity of the separated NP products individually and to scale up the synthesis of the most active catalysts to test for CO oxidation activity.

Research Impact

A total of four students (three graduate, one undergraduate) were directly supported by this funding. 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 these students to the Southeast Regional Meeting of the American Chemical Society (SERMACS) in November 2017 so that they could present their work. For all but one of these students, this was the first time they had attended a professional conference. 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 the chemical reaction mechanisms occurring in PLASMER to the NSF this coming grant cycle.