Development of Nanoplasmonic Mo-Au Photocatalysts for Ammonia Synthesis

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Abstract:

The development of nanoplasmonic molybdenum-doped gold (Mo-Au) photocatalysts incorporated work on the molecular, lab, and systems level scale. On the molecular scale, Mo-Au nanoparticles (NPs) were synthesized through reaction of Au NPs with molybdenum (V) chloride ($MoCl_5$) and $(MoS_2)^{2-}$, respectively. We focused on the synthesis and characterization of Au NPs with $(MoS_2)^{2-}$. The NPs displayed an amorphous shell of $(MoS_2)^{2-}$ around the Au NP as well as a red shift in light absorption. On the lab scale, a reactor was designed and constructed to test the synthesized NPs for their catalytic performance. On the systems level scale, an ASPEN simulation model of an ammonia (NH_3) production process was created to study how pressure and temperature affect utility cost at an industrial scale.
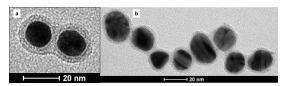
Summary of Research:

The synthesis procedure consisted of two steps: (i) formation of Au NPs and (ii) treatment with Mo. In the first step, Au NPs were synthesized by the addition of a reducing agent, either sodium citrate ($Na_3C_6H_5O_7$) or sodium borohydride ($NaBH_4$), to an Au precursor, gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H20$). The solution was stirred at 80°C for around one hour. In the second step, Mo precursor, either $MoCl_5$ or ammonia tetrathiomolybdate ($(NH_4)_2MoS_2$), was added to the solution of Au NPs synthesized in step 1. The reaction was kept under stirring at 60°C overnight (> 12 hours).

After each step of the synthesis, the NPs were purified via centrifugation (unless otherwise stated). To determine an optimal synthesis strategy in which total synthesis time is minimized while still obtaining a high-quality product, the reducing agent and number of purification steps were varied. The obtained products were compared using UV-vis spectroscopy and transmission electron microscope (TEM) imaging.

UV-vis spectroscopy was used to verify if the final synthesized NPs retained a plasmonic absorbance in the visible region, which is optimal for harnessing solar energy. TEM imaging was used to make qualitative observations about the NPs' morphology, determine average particle size, and verify crystallography with electron diffraction (ED). Additionally, energy dispersive spectroscopy (EDS) with a scanning electron microscope (SEM) was used for an elemental analysis of the NPs.

It was determined necessary to design a lab-scale glass reactor to test the catalytic performance of synthesized Mo-Au NPs. Three parameters were important in the design process: maximize (i) reactant-catalyst interaction, (ii) light transmission, and (iii) ease of setup, takedown, and reloading. Adhering to these parameters, multiple designs were explored in collaboration with David Wise, a glass blower in the Chemistry Department. In the lab-scale set-up, mass flow controllers (MFCs) were used to control H_2 and N_2 reactant gas flow. A white LED was used as light source.

To explore a system-level NH_3 production process that can integrate experimental results from the lab-scale reactor system, a computational model was created using ASPEN. A conventional recycle-stream NH_3 production flowsheet was created by following two published tutorials. The published tutorials provided stream cost, utility costs with heating/cooling values, and simple kinetic model for the reactor. Simulations were run at various operating pressures and temperatures to study how they affect utility costs.

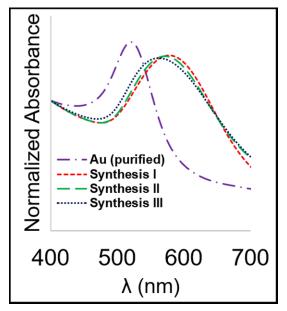*Figure 1: Au NPs with $(MoS_4)^{2-}$ shell from 6-step (a) and 3-step (b) purification method.*
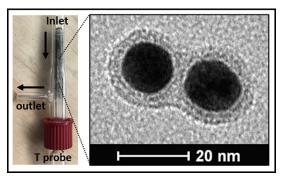

Figure 2: UV-vis of all synthesis methods.
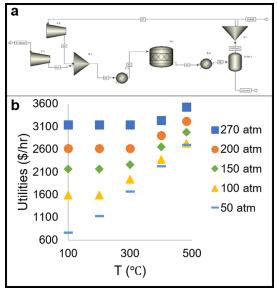

Figure 3: Lab-scale reactor coated with Au-Mo NPs.

Figure 4: ASPEN model of NH_3 production (a) and utilities cost at various operating conditions (b).

Results and Conclusions:

Due to better chemical bonding of S to Au, we quickly realized that Au NPs coated with a $(MoS_2)^{2-}$ shell was our desired Mo-Au catalyst. The most uniform sample of Mo-Au NPs was obtained using $Na_3C_6H_5O_7$ and performing three purifications after each step of the synthesis (Figure 1a). Although the purification process adds to the total synthesis time, it minimizes the size distribution of the final particles. However, due to the lengthy synthesis time (five days), we explored omitting the first three purification steps. This resulted in NPs with the Mo-containing shell in only one day (Figure 1b). However, the NPs were not as uniform in size. Therefore, it was concluded that the first purification step is important because it removes excess reducing agent. Thus, the optimal synthesis strategy involved one initial purification step to remove excess $Na_3C_6H_5O_7$ before adding $(NH_4)_2MoS_2$ and performing the final purification process. The total synthesis time for this procedure was about two days. All synthesis strategies produced NPs that showed a plasmonic absorbance in the 550-600 nm region and a red shift from the 521 nm peak of pure Au NPs (Figure 2). Additionally, the synthesized NPs were observed to aggregate while in solution over a period of days after having been synthesized, which is characteristic of plasmonic peak broadening and color change.

A 5 mm diameter quartz glass reactor that fulfilled all three design parameters was constructed. The "screw-top" design made it easy to coat the outside of the quartz thermocouple well and "screw-in" into position (Figure 3). When testing is complete, the reactor can simply be unscrewed, washed, re-coated, and reloaded. The outlet stem fed directly into an NH_3 gas detector. The created ASPEN model was used to generate a general relationship between operating conditions (P,T) and utility cost (Figure 4).

Future Work:

Using the optimized synthesis procedure, batches of Mo-Au NPs will be synthesized with varying concentrations of $(MoS_2)^{2-}$. The catalytic activity of the NPs will be tested in the lab-scale reactor system. The lab-scale results will be used to inform a kinetic model and operating conditions that more accurately describe our novel photocatalytic process. The model will be used to compare the energetics and cost of conventional and novel NH_3 production processes.

Acknowledgements:

References:

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