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Metal Nanoshells for Plasmonically Enhanced Solar to Fuel Photocatalytic Conversion

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Final Report

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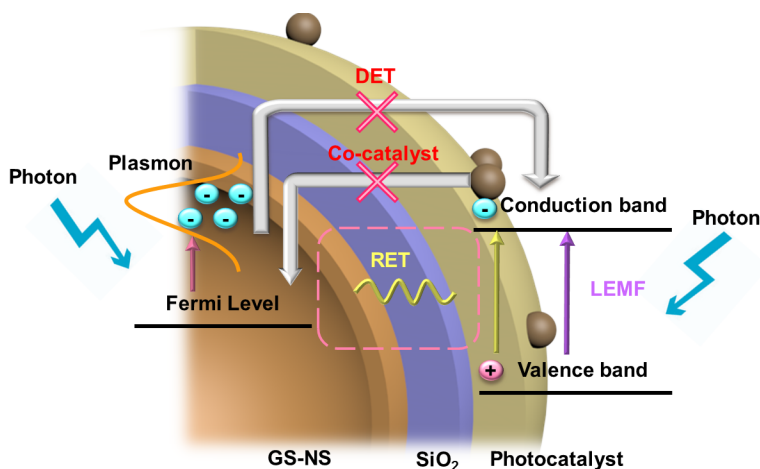
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14. ABSTRACT First thrust: Gold-silver nanoshells (GS-NSs) that provide a tunable localized surface plasmon resonance (LSPR) were prepared for incorporation into a photocatalytic matrix to facilitate charge separation of photo-excited carriers. Zinc indium sulfide (ZIS), a visible light-active photocatalyst, was used as the photocatalytic matrix. In addition, a dielectric interlayer of silica between the GS-NSs and ZIS was used to provide an additional parameter to distinguish the enhancement mechanism. In an extensive study using ten different samples, we found that GS-NS@ZIS particles with an LSPR absorption at ~700 nm and a silica interlayer of ~17 nm generated a rate of hydrogen production 2.6 times higher than that of unmodified ZIS. Second thrust: Tin oxide-coated gold-silver nanoshells were prepared as an alternative plasmonic enhancement system to the silicon oxide system described above. Tin oxide is an attractive material for photocatalytic reactions due to its exceptional photostability and good carrier mobility; however, instead of blocking direct electron transfer, we anticipate this interlayer will modulate charge transfer from the metal to the semiconductor and vice versa. These new core-shell particles were sent to our collaborator, Prof. Tai-Chou Lee at NCU in Taiwan, for evaluation.					
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In the set of experiments pursued under this grant, gold-silver nanoshells (GS-NSs) that provide a tunable localized surface plasmon resonance (LSPR) were used to boost the yield of photocatalytically generated hydrogen from water. A manuscript detailing the work on this project was initially submitted to *ACS Applied Materials & Interfaces* in mid 2015, but the reviewers requested extensive additional experimental work, which delayed peer-reviewed publication until this spring.¹ For this study, composite nanostructures were prepared starting with the GS-NS cores, which were then coated with a thin layer of silica (SiO_2), followed by a zinc indium sulfide (ZnIn_2S_4 ; ZIS) semiconductor shell. The blended-metal GS-NS cores were employed to facilitate charge separation of photo-excited carriers within the surrounding ZIS matrix. The LSPR property of the nanoshells (i.e., the ability of the metals to absorb photons that are in resonance with the frequency of the conduction band electrons of the metal) leads to a redistribution of the absorbed energy via various dissipative mechanisms. This energy transfer can enhance the photoactivity of the system because ZIS is a visible light-active photocatalyst, which for our experiments was synthesized as a ZIS matrix with a band gap of ~ 2.25 eV, producing an extrapolated absorption edge in its UV-visible spectrum of ~ 550 nm.

The three types of GS-NS cores that we prepared and tested exhibited intense extinctions at ~ 500 , 700, and 900 nm, providing a boost in energy to the system. The thicknesses of three different SiO_2 interlayers (~ 17 nm, ~ 42 nm, or no SiO_2) between the GS-NSs and the ZIS photocatalyst provided a means of comparing dielectric barrier properties that helped determine the energy-transfer mechanism(s) that were active for this system. In particular, the direct transfer of hot electrons from the LSPR-activated GS-NSs to the ZIS photocatalyst was blocked by the silica interlayer. Overall, ten samples were prepared, with the highest H_2 gas evolution rate observed for GS-NS particles having an SPR extinction peak at ~ 700 nm and a SiO_2 interlayer thickness of ~ 17 nm; importantly, the rate of H_2 production was 2.6 times higher than that of ZIS with no GS-NSs. These studies (1) demonstrate the existence of coupling between the SPR of the GS-NSs and the absorption of light by ZIS and (2) show that the presence and thickness of the silica interlayer provides key parameters for optimizing solar-based hydrogen production. Therefore, the recent publication of these results provides useful information for the design of plasmon-enhanced photocatalysts for generating H_2 from water.¹

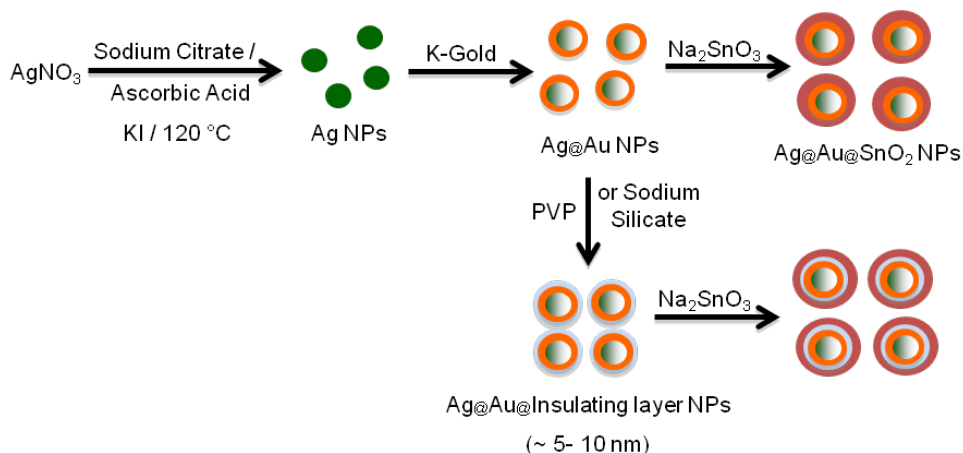
Scheme 1. Illustration of Energy Transfer Mechanisms for SiO_2 -Coated GS-NSs in a ZIS Matrix



In the second set of experiments pursued under this grant, we developed two synthetic approaches for preparing tin oxide-coated gold-silver nanoshells, as illustrated in Scheme 2. These particles were synthesized to compare the performance of these unique nanoshells to that of the first-generation silica-coated GS-NSs in our ZIS photocatalytic system. Tin oxide is a promising coating material for photocatalytic reactions due to its exceptional photostability and good carrier mobility; however, the latter feature means that the coating will play a slightly different role in our composite particle system. Instead of blocking direct electron transfer, we anticipate that thin shells derived from tin oxide and doped tin oxides will modulate charge transfer from the metal to the semiconductor and vice versa. We believe that this alternative shell architecture can further enhance the efficiency of the photocatalytic reactions occurring in the surrounding photocatalyst matrix. Studies of this system will also allow us to develop a better understanding of the fundamental mechanisms occurring within this composite particle system via direct comparisons to the composite particles containing silica-coated GS-NSs.

Additionally, we previously reported that tin oxide-coated gold nanoparticles are markedly more stable than silica-coated gold nanoparticles over a wide range of pH values (*ACS Appl. Mater. Interfaces* **2013**, 5, 2479). Such an improvement in stability not only offers alternative routes to the synthesis of our composite photocatalytic particles, but also offers functional particle architectures under extreme conditions (e.g., high pH). Samples of this new type of core-shell particle have been shipped to our collaborator, Professor Tai-Chou Lee, at National Central University in Taiwan, along with other particles of equivalent light absorptions that are either silica-coated or non-coated, for further testing using the ZIS photocatalyst.² Synthetic procedures for preparing doped versions of these tin oxide-coated nanoshells using antimony, indium, and zinc as dopants are also being pursued, but are still under development.

Scheme 2. Strategy for the Synthesis of Tin Oxide-Coated Gold-Silver Nanoshells



Publication List:

1. Li, C.-H.; Li, M.-C.; Liu, S.-P.; Jamison, A. C.; Lee, D.; Lee, T. R.; Lee, T.-C. Plasmonically Enhanced Photocatalytic Hydrogen Production from Water: The Critical Role of Tunable Surface Plasmon Resonance from Gold-Silver Nanoshells. *ACS Appl. Mater. Interfaces* **2016**, just accepted manuscript. DOI: 10.1021/acsami.6b01197
2. Li, C.-H.; Kolhatkar, A.; Jamison, A. C.; Lee, T.-C.; Lee, T. R. Tunable Plasmonic Core@Shell Nanostructures, manuscript in preparation.