FINAL REPORT

a. DOE Award # and name of the recipient (Institution).

Award#:	DE-SC0002247
Institution:	University of California

b. Project title and name of the PI (and co-PIs, if any).

Title:	"SISGR - Design and Characterization of Novel Photocatalysts With Core-Shell Nanostructures"
PI:	Prof. Francisco Zaera
Co-PIs:	Prof. Christopher J. Bardeen
	Prof. Yadong Yin

c. Date of the report and research period covered by the report.

Date:	March 15, 2017
Period covered:	September 15, 2012 to July 14, 2016

d. A brief description of accomplishments from the DOE award. Use an appropriate format to indicate progress.

Synthesis: we set ourselves to develop different synthetic strategies for the preparation of TiO_2 hollow shells with well-controlled crystallinity, phase, and porosity. In photocatalysis in particular, these structures can provide high active surface area, reduced diffusion resistance, and improved accessibility to reactants. Several synthetic methods have been reported to create TiO_2 hollow shells, typically though ripening or templating processes. Hydrothermal treatments are often used for preparing crystalline TiO_2 hollow shells, either with or without the use of additional sacrificial templates. However, as with many other hydrothermal reactions, these processes are simple and convenient but are usually carried out under high pressures in sealed reactors, and under such conditions it is difficult to monitor the growth and precisely control the shell thickness, porosity, and crystallinity of the products.

We first developed a robust sol-gel coating procedure for producing amorphous TiO_2 shells on templates such as SiO_2 colloids. To produce mesoporous crystalline shells, we have also developed a “silica protected calcination” process that relies on an additional silica coating to limit the structural rearrangement of titania during calcination. We have also studied the causes for the failure of the prior etching and calcination scheme, and designed a new simpler yet robust process for producing uniform mesoporous TiO_2 shells

with highly controllable crystallinity and phases. The key finding of this work is that the base etching of amorphous titania leads to the formation of sodium titanate species which, if not removed, crystallize substantially during calcination and destroy the structural integrity of the TiO_2 shells. We demonstrated the synthesis of anatase titania microspheres with controllable grain sizes by impregnating the porous networks of amorphous titania microspheres with silicate oligomers through the addition and hydrolysis of the precursor tetraethyl orthosilicate and calcining the obtained composite. We have improved our initial synthesis of metal/TiO_2 core/shell composite nanostructures. A controlled sol–gel process has been recently developed to directly coat gold nanoparticles with a relatively thin layer of TiO_2 to produce Au@TiO_2 core–shell catalyst particles, which can be rendered crystalline via calcination at high temperatures. The synthetic strategy for hollow TiO_2 shells has been extended to other catalytically relevant oxides such as zirconium. We have also developed a photocatalytic strategy for the synthesis of colloidal Ag-TiO_2 nanorod composites, in which each TiO_2 nanorod contains a single Ag nanoparticle on its surface. We have studied the contribution of the hollow geometry to the enhancement in photocatalysis. We have explored the use of photocatalyst for designing a novel photoreversible color switching system.

Photophysical and photocatalytic characterization: The spectroscopic and photocatalytic properties of a series of Au@TiO_2 yolk-shell nanostructures were characterized in some detail. In particular, the crystallinity of the TiO_2 shells was varied by changing the etching and calcination conditions. Measurements of the photoluminescence, transient absorption, and H_2 production rate permit us to look for correlations between the spectroscopic and catalytic behavior. We identified clear correlations among the lifetime of the fluorescence decay, the rate at which hydrogen is produced in photocatalysis, and the crystallinity of the titania shells using well-defined Au@Void@TiO_2 yolk-shell nanostructures. The enhancement in photocatalytic activity resulting from adding metals to semiconductor photocatalysts is commonly attributed to a fast transfer of the excited electrons generated by photon absorption from the semiconductor to the metal, a step that prevents de-excitation back to the ground electronic state. However, the photophysics results suggests an alternative pathway that does not involve electron transfer to the metal but requires it to act as a catalyst for the recombination of the hydrogen atoms made via the reduction of protons on the surface of the semiconductor instead. A number of additional experiments were designed to decouple the two effects in order to determine which one is the most pertinent to photocatalysis. Further studies on the fundamental properties associated with the photocatalytic production of hydrogen from water by metal/semiconductor catalysts were carried out by using Au@Void@TiO_2 yolk-shell nanostructures. Independent control of the geometrical parameters of those nanostructures could be exercised during synthesis, and used to systematically probe their effect on photocatalytic activity. Both shell thickness and shell diameter affect the rate of H_2 production, with thicker and larger shells displaying higher activity. In a separate study, and after the characterization of our initial Au@TiO_2 samples reported last year, we used a similar time-resolved photoluminescence approach to investigate the electronic states of hydrogen-treated TiO_2 nanowires.

Mass Transport and Catalytic Performance: The accessibility of the metal nanoparticles in our Metal@TiO_2 nanostructures by reactants for catalysis was assessed by in-situ transmission infrared absorption spectroscopy (IR) using carbon monoxide as a probe. Gold/titania catalysts have also been determined to be good at promoting room-temperature oxidation reactions as long as the Au is in nanoparticle form. We have been exploring this behavior with our well-defined samples. We initiated this investigation with Au@Void@TiO_2 yolk-shell samples, but have now extended it to more standard Au/TiO_2-P25 samples. We have identified a unique gold/titania-based catalyst that, in addition to such room-temperature catalysis, displays a second active regime at much lower temperatures, as low as 120 K. We show that this new catalytic regime follows a mechanism different to that operative at room temperature, and involves at least three titania-adsorbed CO species and a synergy between the CO and O_2 uptakes on the surface. New titanate sites, formed upon treatment of regular Au/TiO_2 catalysts with NaOH, appear to be responsible for the opening of this new reaction channel.

e. A list of papers (mark as published, in press, or submitted) in which DOE support is acknowledged. Attach copies of manuscripts that have been prepared but not yet submitted for publication.

(Only the papers fully supported by this DOE grant are listed:

1. "The effects of photochemical and mechanical damage on the excited state dynamics of charge-transfer molecular crystals composed of tetracyanobenzene and aromatic donor molecules," R. J. Dillon and C. J. Bardeen, *J. Phys. Chem. A* **115**, 1627-1633 (2011).
2. Ilkeun Lee, Ji Bong Joo, Yadong Yin and Francisco Zaera, A New Yolk@Shell Nanoarchitecture for Au/TiO_2 Catalysts, Angew. Chem., Int. Ed., 50(43), 10208–10211 (2011). INVITED
3. "Time-resolved studies of charge recombination in the pyrene/TCNQ charge-transfer crystal: evidence for tunneling," R. J. Dillon and C. J. Bardeen, *J. Phys. Chem. A*, **116**, 5145-5150 (2012).
4. Ji Bong Joo, Qiao Zhang, Ilkeun Lee, Michael Dahl, Francisco Zaera, and Yadong Yin, Mesoporous Anatase Titania Hollow Nanostructures though Silica-Protected Calcination, Adv. Funct. Mater., 22, 166-174 (2012).
5. Ji Bong Joo, Qiao Zhang, Michael Dahl, Ilkeun Lee, James Goebl, Francisco Zaera, and Yadong Yin, Control of the Nanoscale Crystallinity in Mesoporous TiO_2 Shells for Enhanced Photocatalytic Activity, Energy Environ. Sci., 5, 6321-6327 (2012).
6. Dillon, R. J.; Joo, J. B.; Zaera, F.; Yin, Y.; Bardeen, C. J. Correlating the excited state relaxation dynamics as measured by photoluminescence and transient absorption with the photocatalytic activity of Au@TiO_2 core-shell nanostructures. *Phys. Chem. Chem. Phys.*, **2013**, *15*, 1488-1496.

7. Ji Bong Joo, Qiao Zhang, Michael Dahl, Francisco Zaera, Yadong Yin, Synthesis, Crystallinity Control, and Photocatalysis of Nanostructured TiO_2 Shells, J. Mater. Res., 28(03), 362–368 (2013).
8. Ji Bong Joo, Ilkeun Lee, Michael Dahl, Geondae Moon, Francisco Zaera, Yadong Yin, Controllable Synthesis of Mesoporous TiO_2 Hollow Shells: Toward an Efficient Photocatalyst, Adv. Func. Mater., DOI: 10.1002/adfm.201300255 (2013).
9. Qiao Zhang, Ilkeun Lee, Ji Bong Joo, Francisco Zaera and Yadong Yin, Core-Shell Nanostructured Catalysts, Acc. Chem. Res., **46(8)**, 1816–1824 (2013). INVITED
10. Ji Bong Joo, Ilkeun Lee, Michael Dahl, Geondae Moon, Francisco Zaera, Yadong Yin, Controllable Synthesis of Mesoporous TiO_2 Hollow Shells: Toward an Efficient Photocatalyst, *Adv. Func. Mater.*, **23(34)**, 4246-4254 (2013).
11. Ji Bong Joo, Michael Dahl, Na Li, Francisco Zaera, Yadong Yin, Tailored Synthesis of Mesoporous TiO_2 Hollow Nanostructures for Catalytic Applications, *Energy Environm. Sci.*, **6**, 2082-2092 (2013). INVITED
12. Ji Bong Joo, Austin Vu, Qiao Zhang, Michael Dahl, Minfen Gu, Francisco Zaera, and Yadong Yin, A Sulfated ZrO_2 Hollow Nanostructure as an Acid Catalyst in the Dehydration of Fructose to 5-Hydroxymethylfurfural, *ChemSusChem*, **6(10)**, 2001-2008 (2013).
13. Ji Bong Joo, Qiao Zhang, Michael Dahl, Francisco Zaera, Yadong Yin, Synthesis, Crystallinity Control, and Photocatalysis of Nanostructured TiO_2 Shells, *J. Mater. Res.*, **28**, 362-368 (2013).
14. Ji Bong Joo, Robert Dillon, Ilkeun Lee, Yadong Yin, Christopher J. Bardeen and Francisco Zaera, Promoter of H Recombination as an Alternative Mechanism to Electron Trap for the Role of Metals in the Photocatalytic Production of H_2, *Proc. Nat. Acad. Sci.*, **111(22)**, 7942-7947 (2014).
15. Ilkeun Lee and Francisco Zaera, Catalytic Oxidation of Carbon Monoxide at Cryogenic Temperatures, *J. Catal*, **319**, 155–162 (2014).
16. Wang, W.; Ye, M.; He, L.; Yin, Y. Nanocrystalline TiO_2-Catalyzed Photoreversible Color Switching. *Nano Lett.* **2014**, *14*, 1681-1686.
17. Ji Bong Joo, Hongyan Liu, Yoon-Jae Lee, Michael Dahl, Hongxia Yu, Francisco Zaera, Yadong Yin, Tailored Synthesis of C@TiO_2 Yolk-Shell Nanostructures for Highly Efficient Photocatalysis, *Catal. Today*, **264**, 261-269 (2016). INVITED
18. Ilkeun Lee, Ji Bong Joo, Yadong Yin, and Francisco Zaera, Au@Void@TiO_2 Yolk-Shell Nanostructures as Catalysts for the Promotion of Oxidation Reactions at Cryogenic Temperatures, *Surf. Sci.*, **648**, 150-155 (2016). INVITED, Special Issue honoring Gabor A. Somorjai.
19. Yoon Jae Lee, Ji Bong Joo, Yadong Yin, and Francisco Zaera, Evaluation of the Effective Photoexcitation Distances in the Photocatalytic Production of H_2 from Water using Au@Void@TiO_2 Yolk-Shell Nanostructures, *ACS Energy Lett.*, **1** (2016) 52-56. INVITED, Inaugural Issue.

f. A comprehensive list of people working on the project – graduate students, postdocs, visitors, technicians, etc. Indicate for each the percentage of support obtained from the grant.

Graduate Students:	Robert Dillon, Qiao Zhang, Michael Dahl, Zhenda Lu, James Goebl, Le He, Xiaoliang Liang, Jie Li
Postdocs:	Dharma Kurunthu, Ilkeun Lee, Ji Bong Joo, Chuanbo Gao, Yoon Jae Lee, Kerry Hanson, Geondae Moon, Wang Wenshou

g. Estimate of the unexpended funds at the end of the final budget period; if funds exceed 10% of the annual budget, provide a detailed explanation.

No balance left, all funds were spent.