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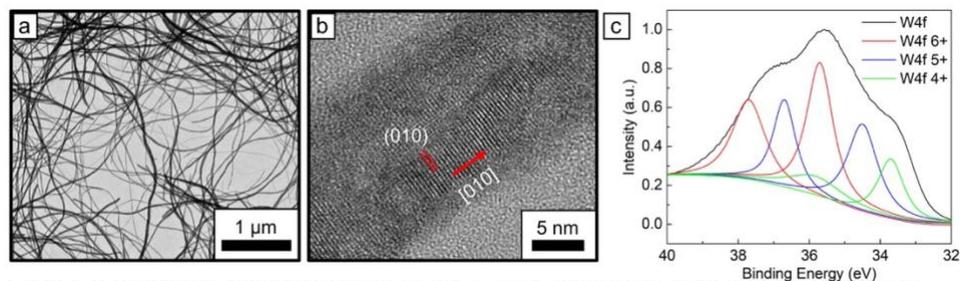
Project title: Identification of Active Sites in Methane Oxidation Catalysts by Single-Molecule Fluorescence Imaging

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The goal of this project is to apply single-molecule fluorescence microscopy to image nanoscale variations in catalytic activity for metal oxide photocatalysts. We originally proposed to conduct these studies on bismuth vanadate microcrystals, as these particles can photocatalytically convert methane to methanol.¹ However, during the first year of the project period we determined that tungsten oxide is a more suitable photocatalyst for our studies. We observed that the bismuth vanadate microcrystals produced a large background emission under laser excitation with the fluorescence microscope. This background limits the precision to which redox-active fluorogenic probes can be localized on the surface of the crystals. We then synthesized tungsten oxide nanowires that do not fluoresce, and we are able to map variations in catalytic activity along the lengths of these nanowires. Similar to bismuth vanadate, tungsten oxide powders have shown high photocatalytic activity for CH_4 to CH_3OH conversion.² Thus, the knowledge gained from our current studies on tungsten oxide has relevance for converting natural gas into a liquid product.

Tungsten oxide nanowires were prepared using solvothermal synthesis. Transmission electron microscopy (TEM) shows the nanowires have lengths on the order of tens of microns and diameters between 5 and 30 nm (**Figure 1a**). X-ray diffraction patterns of the nanowires match the monoclinic phase of $\text{W}_{18}\text{O}_{49}$ (data not shown). A high-resolution TEM image (**Figure 1b**) of a single nanowire indicates the nanowire grew along the [010] direction. The monoclinic crystal structure corresponding to $\text{W}_{18}\text{O}_{49}$ can accommodate small variations in the W:O stoichiometry that arise due to oxygen vacancies. X-ray photoelectron spectroscopy (XPS) shows that W ions in the nanowires exist in the +6, +5, and +4 oxidation states (**Figure 1c**), which indicates the presence of oxygen vacancies for charge balance.

Under photoexcitation with light above the band gap of tungsten oxide (~ 2.8 eV), photogenerated holes in the valence band are able to oxidize water to generate hydroxyl radicals ($\bullet\text{OH}$). Hydroxyl radicals are a critical intermediate in the oxidation of CH_4 to produce CH_3OH .¹⁻² While the catalytic



a) Low-magnification TEM image of a bundle of $\text{W}_{18}\text{O}_{49}$ nanowires. b) High-resolution TEM image of a single nanowire showing (010) lattice planes of $\text{W}_{18}\text{O}_{49}$ perpendicular to the nanowire length. c) XPS spectrum for $\text{W}_{18}\text{O}_{49}$ nanowires in the binding energy region for W 4f electrons

activity of tungsten oxide is highly dependent upon the presence of structural defects, such as oxygen vacancies,³ the spatial variation in activity for individual particles has not been measured. To image variations in the activity along individual nanowires we used single-molecule fluorescence microscopy and a redox-active probe molecule that becomes highly fluorescent after reaction with $\bullet\text{OH}$ radicals. Hydroxyl radicals can cleave the aminophenyl group of 3'-(p-aminophenyl) fluorescein (APF) to generate fluorescein (**Figure 2a**). As APF is non-fluorescent while fluorescein is highly fluorescent, we can image individual turnovers for this reaction and localize them with nanoscale precision using localization algorithms developed for super-resolution imaging. By localizing the generation of many fluorescein molecules over time by an individual nanowire, we create an activity map along the length of the nanowire. One such activity map is shown in **Figure 2c** in which we observe significant variations in photocatalytic activity along the length of the nanowire. This map required simultaneous illumination with a 405 nm laser to excite the tungsten oxide nanowire and a 488 nm laser to excite the fluorescein product. Similar variations in activity were observed in a dozen other nanowires.

As noted by one of the reviewers for this proposal, the nanoscale resolution provided by this technique still averages over hundreds of atoms on the surface of the catalyst. Thus, to obtain further information on the chemical nature of the sites that produce $\bullet\text{OH}$ radicals, we used a second fluorogenic reaction, the condensation of furfuryl alcohol (**Figure 2b**). This second reaction is catalyzed by Lewis acidic sites on the surface of tungsten oxide and does not require photoexcitation. As shown in **Figures 2d** and **2e**, qualitatively there is significant overlap between the regions of the nanowires that are active for generating fluorescein and the regions that catalyze condensation of furfuryl alcohol. When we add a ligand that binds to Lewis acidic sites on the surface of the nanowires, the overlap

between activity maps made by the two probe molecules decreases. We are currently working to better quantify the degree of overlap between the two images. These results indicate that Lewis acidic sites which arise from oxygen vacancies on the surface of the nanowires are the catalytically active sites for both the oxidation of water to create $\bullet\text{OH}$ radicals and the condensation of furfuryl alcohol. In future work, we will image variations in activity for tungsten oxides nanowires after different chemical treatments to change the concentration of oxygen vacancies. We hypothesize that the activity of the nanowires for CH_4 to CH_3OH conversion may be enhanced by increasing the number and uniformity of acidic sites along the tungsten oxide nanowires

As PI for this project, I received partial support for one summer month. I have presented results from this project during invited talks at Temple University, Nanjing University, Fudan University, and the Hong Kong University of Science & Technology. A portion of the results from this project were essential preliminary data in a recently awarded grant from the National Science Foundation (CHE-1753344 NSF CAREER). The five-year NSF grant will take this research in a new direction by using high-resolution transmission electron microscopy to image structural defects in photocatalyst particles and correlate the locations of those defects with activity maps obtained from single-particle, super-resolution imaging.

Funds from this grant were used to support the research of two graduate students and one undergraduate student.

One graduate student, currently in his 4th year of graduate school, was supported for the entire year of the project period. He conducted the single-molecule, super-resolution studies described above. Travel funds were used for this student to give a talk at the Gordon Research Seminar on Colloidal Semiconductor Nanocrystals. This was the first time that he presented his research outside of Washington University, and he received valuable feedback on his project. He also plans to obtain a postdoctoral research position following his PhD, and this conference provided an opportunity to meet with potential postdoctoral sponsors. A second graduate student, currently in his second year, was supported for 1.5 months during the summer of the project period. During this time, the student learned how to synthesize metal oxide particles and measure their photocatalytic activity for methane to methanol conversion. These measurements will enable us to compare the activity of individual tungsten oxide nanowires to the average photocatalytic activity of the ensemble. An undergraduate student at Washington University was also supported for 10 weeks during the summer of the project period. He is currently a junior, and last summer was his first experience in scientific research. The oxidative APF probe that is being used in the studies described above is commercially available. However, based on limitations in the stability and quantum yield for commercially available reductive probes, the undergraduate student is synthesizing a boron dipyrromethene dye to image reduction events catalyzed by the same tungsten oxide nanowires. He has almost completed this synthesis, and he is continuing his research during the academic year for course credit. As this student is highly interested in pursuing a PhD in chemistry, I believe the opportunity to perform undergraduate research will be a highly valuable experience when he applies to graduate school.

References. (1) Murcia-López, S.; Villa, K.; Andreu, T.; Morante, J. R., Partial Oxidation of Methane to Methanol Using Bismuth-Based Photocatalysts. *ACS Catalysis* **2014**, *4*, 3013-3019. (2) Taylor, C. E.; Noceti, R. P., New Developments in the Photocatalytic Conversion of Methane to Methanol. *Catalysis Today* **2000**, *55* (3), 259-267. (3) Zhang, N.; Li, X.; Ye, H.; Chen, S.; Ju, H.; Liu, D.; Lin, Y.; Ye, W.; Wang, C.; Xu, Q.; Zhu, J.; Song, L.; Jiang, J.; Xiong, Y., Oxide Defect Engineering Enables to Couple Solar Energy into Oxygen Activation. *Journal of the American Chemical Society* **2016**, *138* (28), 8928-8935.

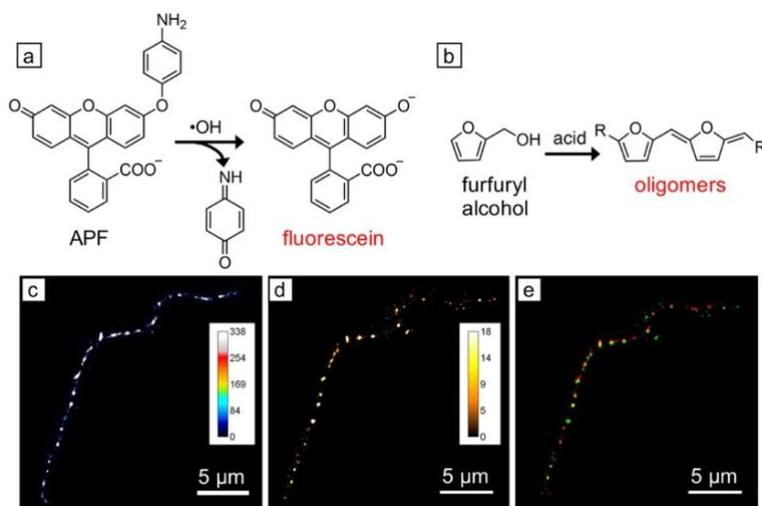


Figure 2. Single-molecule imaging of catalytic activity with fluorogenic probes. a) APF reacts with hydroxyl radicals to produce fluorescein. b) The acid-catalyzed condensation of furfuryl alcohol produces fluorescent oligomers. c) Super-resolution map showing the locations where fluorescein was generated on a single $\text{W}_{18}\text{O}_{49}$ nanowire under dual 405 and 488 nm excitation. d) Super-resolution map for the same nanowire but using furfuryl alcohol and 561 nm excitation. The color scales in both c) and d) indicate the number of fluorescent molecules detected in a given region. e) Overlay of images c) and d).