Introduction
Photocatalytic water splitting to produce hydrogen was first studied on TiO$_2$ [1], which suffers from poor light absorption and cannot absorb light in the visible range. Recently, researchers have combined plasmonic metals with TiO$_2$ in order to increase light absorption [2, 3]. Although, the optical properties of these composite materials have been well characterized, there is still a lack of information on the catalytic mechanisms occurring in these systems. Since oxygen evolution is the rate-limiting process in water splitting to produce hydrogen [4], we aim to better understand the mechanism of this reaction on TiO$_2$ and TiO$_2$/Au. We believe that the catalytic behavior of the system will be dependent upon the light excitation wavelength, which can be classified into a few basic regimes—UV light, visible light in the Au interband region, and visible light in the Au surface plasmon resonance (SPR) region. Under UV light in a pure TiO$_2$ system, the excitation of an electron hole pair and the subsequent hole-driven chemistry will occur on TiO$_2$, where the creation of holes will be spatially diffuse and relatively far from the surface where chemistry occurs. When Au is excited with light that matches its SPR, strong enhanced electromagnetic fields could both enhance and localize hole creation near the reactive interface. Therefore, we propose that oxygen evolution on SPR-excited Au may be more efficient than oxygen evolution on TiO$_2$ due to easier access of adsorbates to holes.

Materials and Methods
We synthesize TiO$_2$/Au composites using a deposition-precipitation method [2]. Briefly, we heat water to 70°C, add gold (III) chloride in dilute hydrochloric acid, adjust the pH above 9 using 0.1 M NaOH, and then add P25 TiO$_2$. After stirring for 4 hours, we wash the catalyst and calcine in air at 200°C for 4 hours. To test the activity of the catalysts for water splitting, we do photoelectrocatalytic oxygen evolution. We use a three-electrode cell with 1 M KOH electrolyte. During the experiment, we constantly deaerate with Ar to prevent unwanted back reactions. With a potentiostat, we control the potential and measure current as a proxy for oxygen evolution activity.

Results and Discussion
Using photoelectrochemical methods, we compare the water-splitting activity of TiO$_2$ and TiO$_2$/Au under the various light regimes. By measuring their activity as a function of light intensity and as a function of temperature, we propose to explore the characteristics of the holes involved in the reaction including their origin, mobility and localization.

Figure 1. Left: TEM image of Au nanoparticles on TiO$_2$. Average diameter of Au nanoparticles is 3nm +/- 2nm. Right: Photograph of a TiO$_2$/Au film on a glass slide.

Significance
Solar water splitting offers a renewable, carbon-free way to meet the world’s energy needs by producing hydrogen fuel. Currently the process is limited by the slow kinetics of the oxygen evolution reaction. Plasmonic metals have been proposed as ways to better capture the light, but thus far relatively little work has been done on understanding the mechanism of oxygen evolution on composite plasmonic metal/semiconductor systems.

References