Plasmonic metal nanostructures for solar water splitting and light-driven selective partial oxidation of olefins

Andiappan Marimuthu, Phil Christopher, Hongliang Xin, S. Linic*
University of Michigan, Ann Arbor, MI 48109 (USA)
*linic@umich.edu

Introduction
Plasmonic nanoparticles of noble metals are characterized by their strong interaction with UV-vis light through an excitation of localized surface plasmon resonance (LSPR). The excitation of LSPR is manifested in very high oscillating electric fields localized in the neighborhood of illuminated nanostructures (the light is concentrated in the neighborhood of the nanostructure) and high rates of the formation of energetic charge carries (high energy electrons) on the nanostructure. I will illustrate how we take advantage of this strong interaction of UV-vis light with these metallic nanostructures to drive a number of photo-catalytic processes, including water splitting and selective partial oxidation reactions (2). I will discuss underlying mechanisms (2).

Materials and Methods
Metallic nanostructures were prepared using conventional colloidal methods. Organic stabilizers (mainly PVP) were used to direct the growth and shape of the nanostructures. Photo-catalytic activity for the water splitting reaction was measured in a three-electrode cell with 1 M KOH electrolyte in a deaerate solution. The partial oxidation reactions were performed in a vertically oriented reactor that allows both temperature control and catalyst illumination. We used a visible light source with a total maximum intensity of ~ 250 mW/cm² (2–3 times solar intensity) at the entrance of the catalyst bed and maximum spectral intensity at ~2.1 eV (590 nm).

Results and Discussion
In the first example, we will show that illuminated plasmonic nanoparticles of Ag in proximity of a semiconductor (we used N-doped TiO2) can enhance significantly the rate of photocatalytic water splitting on the semiconductor (Fig. 1a).(2,4) We demonstrate that the critical rate enhancement mechanism involves the radiative transfer of energy from the Ag LSPR to the nearby semiconductor particles, increasing the production of e⁻/h⁺ pairs in the semiconductor. We find that the enhancement of e⁻/h⁺ pair concentration in N-TiO₂ is the highest near the semiconductor particle surface (where the Ag EM fields are strongest). This is significant, as e⁻/h⁺ pairs near the N-TiO₂ surface are more chemically useful, i.e., fewer undergo recombination since they have to diffuse much shorter distances to reach the surface and react. We will discuss our findings in the context of the design of optimal materials for photo-catalytic splitting of water.(2,4)

In the second example, I will show that the illuminated plasmonic nanostructures (essentially nanoparticles of Ag and Cu) can themselves act as photocatalysts. (1,3) Figure 1(b) shows the steady-state rate of partial oxidation of ethylene to form ethylene oxide over 60 nm edge length Ag nanocubes at 450 K and atmospheric pressure, with and without visible light illumination (of the order of solar intensity). Figure 1(b) shows that the steady-state reaction rate increases 4 fold in response to visible light illumination and that this performance is fully reversible. I will discuss the mechanism associated with the observed photocatalysis on metals. The critical feature of the mechanism is that energetic electrons drive the reaction which is fundamentally different that for reactions on metals driven by thermal flux. I will demonstrate how the properties of plasmonic nanostructures can be tuned to design highly selective photo-catalysts for “difficult” chemical transformations. Here, I will mainly focus on propylene epoxidation on plasmonic Cu nanoparticles showing that the illuminated Cu nanoparticles exhibit higher selectivity in this partial oxidation reaction than any other heterogeneous catalyst, Fig 1c.

Figure 1. (a) Rate of water splitting reaction on various materials. Introduction of plasmonic Ag increases the reactions rate considerably. (b) Rate of ethylene epoxidation on plasmonic Ag nanoparticles. Particles illuminated by light exhibit significantly larger rates, consistent with the existence of a photo-chemical reactions channel. (c) Comparison between the selectivity to propylene oxide is propylene epoxidation reactions on Cu nanoparticles (thermal process) with light off, and the same nanoparticles illuminated with low intensity visible light. Optical excitation of Cu with light causes dramatic changes in the selectivity. We will discuss the mechanism associated with this change.

Significance
Efficient harvesting of solar energy and its conversion into chemical energy is one of the most important contemporary problems. We will discuss a class of materials that show great promise in this field.

References