Multifunctional catalysts for solar-driven fuel production and chemical conversion

Phillip Christopher1, Matthew Kale1, John Matsubu1 and Gabriel Gusmao1

1University of California, Riverside. Riverside, CA, 92521 (USA)
Department of Chemical and Environmental Engineering
christopher@engr.ucr.edu

Introduction
In this talk we show examples of rationally designed multifunctional catalysts utilized to reduce thermal requirements of chemical processes and to execute solar-driven conversion of combustion products (CO2+H2O) into fuels. The first example is motivated by our recent discovery that excited Ag surface plasmons can drive direct photocatalytic processes on their surfaces. We show here that bimetallic nano architectures, consisting of plasmonic (Ag) and catalytic (Pt/Ru) functionalities in direct electrical contact, can exploit the strong plasmon concentration of visible photons on Ag to drive photocatalytic processes on the more reactive metal (Pt/Ru) surfaces. In the second example, we have designed a multifunctional system consisting of metallic catalytically active sites that perform photocatalytic H2O splitting and thermocatalytic CO2 methanation (CO2+4H2 → CH4+2H2O) co-localized on a visible light absorbing semiconductor for efficient execution of artificial photosynthesis (AP, CO2+2H2O → CH4+2O2). The results show that, against conventional wisdom, the rates of photocatalytic processes can be significantly enhanced at elevated temperatures.

Materials and Methods
The bimetallic architectures utilized for plasmon driven photocatalysis were synthesized through a sequential approach. Ag nanocubes were first synthesized via the polyol synthesis approach. The catalytically active species (Pt/Ru) were grown on the Ag cubes in aqueous solution by controlling reaction temperature, metal salt addition rate and ascorbic acid (reducing agent) concentration. The multifunctional AP catalysts consist of semiconductors (N-doped TiO2 and solid solution GaN:ZnO) modified through high temperature processing in NH3. Active metal and oxide species were deposited through impregnation and photoreduction approaches. All reactions were executed in a flow through, packed bed reactor that allows concurrent control of temperature and illumination. Illumination was provided by a 1600 W Oriel light source with an AM 1.5 filter coupled to a monochromator and a liquid light guide that is coupled to the reactor.

Results and Discussion
In figure 1(a) we show the rate of thermo- and photocatalytic CO oxidation as a function of operating temperature for 70 nm edge-length Ag nanocubes and 5 wt % Pt on Ag nanocubes (Pt@Ag). The catalysts were illuminated with visible light (400nm-hv~700nm) at an intensity of 300 mW/cm². The Ag cubes showed activity with no light at ~170 °C and a rate enhancement of 2-5 fold due to illumination. The Pt@Ag catalyst showed thermal activity at much lower temperature, 120 °C, and showed significant rate enhancement (2-4 fold) due to visible light illumination. Because the Pt@Ag catalyst showed photocatalytic activity below the temperature where pure Ag showed activity (with or without light) the results indicate that the visible light is inducing photocatalytic activity on Pt. Furthermore, because small Pt particles only have weak plasmon resonance in the UV region and no UV photons were used to excite the catalyst, the results indicate Ag plasmons are excited and transfer energy to Pt, thereby driving photocatalytic reactions on the Pt surface. Wavelength and intensity dependent measurements support these conclusions. Similar results were observed for CO2 methanation driven on bimetallic particles consisting of Ru decorated Ag nanocubes.

To test the effect of temperature on photocatalysis for AP, three monometallic catalysts (Pt, Ru and Rh) were deposited on N-doped TiO2 at weight loadings of 1%. A temperature ramp from 100-300°C in the dark and with solar simulator illumination was performed while H2O saturated CO2 was continuously fed to the reactor at 3 scem. The Pt and Ru based catalysts showed no measurable products in the dark or under illumination for the entire temperature range. On the other hand, figure 1(b) shows that when the Rh/TiO2 catalyst was illuminated, significant CH4 production was observed. The rate of CH4 production at 250 °C is 3 times greater than the current state-of-the-art for solar driven AP. Our results show that light and heat must be supplied to the system to induce activity and CO2 must be used as the reactant to obtain CH4 production. Based on mechanistic analysis of the process we tentatively suggest that the Rh active site can perform dual functionality of a photocatalytic H2 evolution site and as a selective thermocatalytic CO2 methanation site, see Figure 1(c).

Significance
The first example shows that bimetallic architectures consisting of constituents with plasmonic and catalytic functionalities represent a novel class of versatile photocatalytic materials for executing a variety of important chemical reactions at low temperature. The second example shows that the addition of an external thermal stimulus to the AP process can significantly enhance the photocatalytic rate of product formation. In general, the results show unique routes towards enhancing the energy efficiency and reducing the environmental impact of current fuels and chemical production processes by allowing lower temperature chemical conversion and solar driven conversion of combustion products into fuels.

References