J Environ Geol. | Volume 3
ISSN: 2591-7641

Hot electron-mediated plasmonic photocatalysis using heterojunctions of noble metal nanoparticles and semiconductors

Karthik Shankar
University of Alberta, Canada

Statement of the Problem: Several industrially relevant catalytic chemical reactions require either high temperature or high pressure or both. A particularly energy intensive reaction is the transformation of CO2 into value-added products. The catalyst - typically a finely divided noble or transition metal/alloy, reduces the activation energy barrier for the chemical reaction, by coupling to the vibrational modes of the reactants. Achieving sustainability involves making these reactions more energy efficient by reducing the thermal budget required. A stretch goal is to be able to run the majority of industrial chemical reactions close to room temperature using renewable energy.

Methodology & Theoretical Orientation: Plasmonic photocatalysis offers the promise of using light as the energy source to drive a variety of chemical reactions close to room temperature. Surface plasmons are quantized collective oscillations of the electrons in noble metal nanostructures that strongly interact with visible and near-infrared photons. Ultrafast decay of the plasmons either by Landau damping or chemical interface damping results in the creation of highly energetic carriers called hot electrons that can be used to drive a chemical reaction and thus perform work. However, the hot electrons lose their excess energy thermal equilibrium over the picosecond timescale through a sequence of relaxation processes. We studied noble metal-semiconductor heterojunctions as platforms to utilize hot electrons before their relaxation.

Findings: TiO2-Au nanoparticle (NP) heterojunctions were found to be particularly effective in driving CO2 reduction and photoelectrochemical water-splitting due to extremely long-lived photoelectrons, which were formed by the ultrafast injection of hot electrons from Au NPs into the conduction band of TiO2 across a Schottky barrier. Likewise, heterojunctions of graphenic semiconductors (e.g g-C3N4, C3N5) with Ag nanoparticles were excellent for driving surface reactions and effluent degradation under visible illumination.

Conclusion & Significance: Hot electron injection into TiO2 nanomaterials appears to be faster than conventional theory would suggest, and the resulting charge separation is unusually long-lived. Au NP-TiO2 and Ag NP-graphenic semiconductor are highly promising plasmonic heterojunctions that can potentially photocatalyze a range of important chemical reactions using visible light.

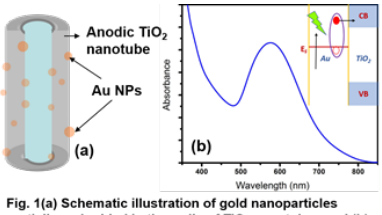

Fig. 1(a) Schematic illustration of gold nanoparticles partially embedded in the walls of TiO_2 nanotubes and (b) their strong LSPR resonance w/inset showing the band diagram for hot electron injection from Au to TiO_2.