<u>CHEM 431 – Additional Experiment</u>
Photoelectrochemical Instrumentation

REFERENCES:

Bard, A.; Faulkner, L. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons: New York, 2001; Chapters 15 and 18

INTRODUCTION:

Electrochemical processes have been utilized in numerous applications, from the purification of aluminum to the polishing of silverware. The current trend in global energy consumption, coupled with the annual incident power density of sunlight on Earth, has been the origin of many innovative projects that rely on the electrochemical activity of semiconductors. Unlike metals, which intrinsically possess large concentrations of easily conductable electrons, semiconductors require an excitation source, excess charge carriers that rely on the Pauli Exclusion Principle to move, or both prior to being able to conduct electricity. In the simplest case, a semiconductor can be excited by absorbing light equal to or greater than the bandgap value to promote an electron from the valence band to the conduction band. The electron leaves behind a positively-charged entity called a *hole* that can also be used to perform electrochemistry. If the energy required to reduce a species in solution is *less than* the energy of the conduction band, the reduction can occur. Similarly, if the energy required to oxidize a species in solution is *greater than* the energy of the valance band, the oxidation can occur. However, without the charge carriers first being separated, no electrochemical processes will occur.

POTENTIOSTAT:

The instrumentation involved in electrochemical studies is some of the most electronically simple that you may encounter in the research lab. Refer to the PDFs that have been posted on RamCT for an indication of what circuitry is required. The potentiostat is built primarily from three Operational Amplifiers (OpAmps) that are connected through “wires” composed of the electrodes and a conductive solution that surrounds them. Other instrumentation is valuable, such as a sweep generator and integrator, but the only truly necessary component is the potential voltage source. The instrumentation used for this experiment will be computer interfaced, but the same basic electronics are inside.

PROCEDURE:

Prepare a solution of 0.05 M potassium ferricyanide + 0.1 M sodium bicarbonate. The instructor will show you how the computer-interfaced potentiostat works. Using the semiconductor electrode, take voltammetric scans with and without an applied UV excitation source. Using internet resources, find another analyte that either cannot be oxidized or cannot be reduced using the given semiconductor.

DISCUSSION:

Discuss how the potential is maintained at and current flows to and from the working electrode based on how the circuits are “wired” together through the solution. What happened in the absence of UV light when the potential was scanned? Why does it change when the UV light illuminates the electrode?