University of California, Riverside

Bioinspired Engineering for Sustainable Energy
BIEN 166

Lectures: Three-hour lectures per week
One-hour discussion per a week

Text: The course will use selected chapters from the following textbooks: "*Biochemistry*," 6th edition, by J. M. Berg, J. L. Tymoczko, and L. Stryer, "*Molecular Fluorescence*" by B. Valeur, and "*Principles of Fluorescence Spectroscopy*," 3rd edition, by J. R. Lakowicz.

Predominantly, the course is based on peer-reviewed journal publications (reviews and research articles) as outlined in the topic list at the end of the syllabus. The information in the textbooks is usually about 10 to 20 years old (at least). While good textbooks are indispensible sources for some of the established fundamentals, it is the recent peer-reviewed articles that demonstrate the latest discoveries and advances in the fields.

Class notes and handouts:

An outline of the topics follows at the end of this syllabus. With additional handouts that will be distributed in due time, this rough outline of topics will be further broken in terms of book chapters and publications of particular interests and suggested problems and exercises. Concepts in terms of overreaching ideas or paradigms will be built. These paradigms summarized will be distributed as handouts as the course proceeds.

Examinations and grading:

Discussions: students will prepare short presentations on recent publications or governmental energy policy documents and discuss the topics with the rest of the class.

Quizzes: three to ten minute quizzes at the end of the lecture periods will be conducted every week or every two weeks: the quizzes will be on the material covered in the lectures and during the discussions.

Grades will be assigned on the bases of 100 points with the following breakdown:

Discussions	50
Quizzes	50

Objectives of the course:

- To teach students the fundamentals of energy conversion and energy storage.
- To provide the students with **quantitative** understanding of the world energy consumption and energy production trends.
- To teach students how the principals of natural photosynthesis provide the means for advancing the sustainable-energy technologies.
- To teach students the experimental techniques used for studying and for characterization of the photoinduced energy and charge transduction processes.
- To make students appreciate the current challenges in sustainable energy, such as energy storage, photocatalytic water splitting, and carbon-dioxide fixation.
- To demonstrate to students key features of living systems that are still unexplored in engineering, such as self replacement and damage management.
- To provide some training in critical thinking and analysis

Outline of topics and coverage:

(The reading includes the listed publications and the REFERENCES cited in these publications. Because many of the listed peer-reviewed journal publications are review papers, the students will be required to go to the original sources in order to truly comprehend many of the advanced concepts.)

Week 1
Present and projected energy-production and energy-consumption rates
Comparison between energy sources and their potential for sustainability
Carbon-neutral energy sources, such as nuclear, wind, hydro, geothermal and solar
How solar energy has sustained life on Earth, and why solar is the path toward sustainability?

Reading:
- Reports from the US National Commission on Energy Policy.
- Lewis, N. S., "*Toward Cost-Effective Solar Energy Use*," *Science*, 2007, 315, 798–801.
- Barnham, K. W. J.; Mazzer, M.; Clive, B. "*Resolving the Energy Crisis: Nuclear or Photovoltaics?*", *Nature Materials*, 2006, 5, 161-164.
- Gray, H. B., "*Powering the Planet with Solar Fuel*," *Nature Chemistry*, 2009, 1, 7.

Week 2:
Light-matter interaction
Energy harvesting, and energy transduction
Photoinduced charge transfer, transition-state theory, and electron-transfer pathways

Reading:
- Valeur, B. in "*Molecular Fluorescence*," chapters 1 and 2
- Marcus, R. A.; Sutin, N., "*Electron transfers in chemistry and biology*," *Biochim. Biophys. Acta, Rev. Bioenerg.*, 1985, 811, 265-322.
- Beratan, D. N.; Betts, J. N.; Onuchic, J. N., "*Protein Electron Transfer Rates Set by the Bridging Secondary and Tertiary Structure*," *Science*, 1991, 252, 1285-1288.
- Vullev, V. I.; Jones, G., "*Photoinduced Charge Transfer in Helical Polypeptides*," *Res. Chem. Interm.*, 2002, 28, 795-815.
- Jones, G.; Vullev, V. I., "*Photoinduced Electron Transfer between Non-Native Donor-Acceptor Moieties Incorporated in Synthetic Polypeptide Aggregates*," *Org. Lett.*, 2002, 4, 4001-4004.

Week 3 and 4:
Biomimicry, biomimesis and bioinspiration
Fundamentals of photosynthesis
Design of biomimetics and bioinspired light-harvesting systems
Artificial photosynthesis

Reading:
- Vullev, V. I., "*From Biomimesis to Bioinspiration: What's the Benefit for Solar-Energy-Conversion Applications?*", *J. Phys. Chem. Lett.*, 2011, 2, 503-508.
- Berg, J. M.; Tymoczko, J. L.; Stryer, L. in "*Biochemistry*," chapter on photosynthesis.
- Zhou, H., et al., "*Artificial Inorganic Leafs for Efficient Photochemical Hydrogen Production Inspired by Natural Photosynthesis*," *Advanced Materials*, 2010, 22, 951-956.
- Rabanal, F.; DeGrado, W. F.; Dutton, P. L., "*Toward the Synthesis of a Photosynthetic Reaction Center Maquette: A Cofacial Porphyrin Pair Assembled between Two Subunits of a Synthetic Four- Helix Bundle Multiheme Protein*," *J. Am. Chem. Soc.*, 1996, 118, 473-474.
- Cristian, L.; Piotrowiak, P.; Farid, R. S., "*Mimicking Photosynthesis in a Computationally Designed Synthetic Metalloprotein*," *J. Am. Chem. Soc.*, 2003, 125, 11814-11815.
- Steinberg-Yfrach, G.; Rigaud, J.-L.; Durantini, E.N. ;Moore, A. L.; Gust, D.; Moore, T. A., "*Light-Driven Production at ATP Catalyzed by F0F1-ATP Synthase in an Artificial Photosynthetic Membrane*," *Nature*, 1998, 392, 479-482.
- Bennett, I. M., et al., "*Active transport of Ca2+ by an artificial photosynthetic membrane*," *Nature*, 2002, 420, 398-401.

Week 5
Techniques for studying photoinduced processes and light-harvesting systems
Electrochemical methods
Time-resolved spectroscopy

Reading:
- Lakowicz, J. R. in "*Principles of Fluorescence Spectroscopy*," chapters on time-resolved spectroscopy.
- Bao, D., et al., "*Electrochemical Reduction of Quinones: Interfacing Experiment and Theory for Defining Effective Radii of Redox Moieties*," *J. Phys. Chem., B*, 2010, 114, 14467-14479.
- Bao, D., et al., "*Electrochemical Oxidation of Ferrocene: A Strong Dependence on the Concentration of the Supporting Electrolyte for non-Polar Solvents*," *J. Phys. Chem., A*, 2009, 113, 1259–1267.
- Wan, J., et al., "*Solvent Dependence of the Charge-Transfer Properties of a Quaterthiophene-Anthraquinone Dyad*," J. *Photochem. Biotobiol. A: Chemistry*, 2008, 197, 364-374.
- Jones, G.; Vullev, V. I., "*Photoinduced Electron Transfer between Non-Native Donor-Acceptor Moieties Incorporated in Synthetic Polypeptide Aggregates*," *Org. Lett.*, 2002, 4, 4001-4004.

Week 6
Photovoltaics
Nanotechnology for solar-energy devices: quantum-dot sensitized solar cells

Reading:
- Kalyanasundaram, K.; Graetzel, M., "*Artificial Photosynthesis: Biomimetic Approaches to Solar Energy Conversion and Storage*," *Curr. Opin. Biotechnol.*, 2010, 21, 298-310.
- Kamat, P. V. "*Quantum Dot Solar Cells. Semiconductor Nano-crystals as Light Harvesters*," *J. Phys. Chem. C*, 2008, 112, 18737-18753.

Week 7 and 8
Photocatalytic water splitting
Natural water oxidation: photosystem II
Natural and biomimetic hydrogenases
Artificial water splitting: advances and challenges

Reading:
- Loll, B. et al., "*Towards complete cofactor arrangement in the 3.0 A resolution structure of photosystem II*," *Nature*, 2005, 438, 1040-1044.
- Jordan, P., et al., "*Three-dimensional structure of cyanobacterial photosystem I at 2.5 A resolution*," *Nature*, 2001, 411, 909-917.
- Rauchfuss, T. B., "*A Promising Mimic of Hydrogenase Activity*," *Science*, 2007, 316, 553-554.
- Gloaguen, F.; Rauchfuss, T. B., "*Small Molecule Mimics of Hydrogenases: Hydrides and Redox*," *Chem. Soc. Rev.*, 2009, 38, 100-108.
- Dismukes, G. C., et al., "*Development of Bioinspired Mn4O4-Cubane Water Oxidation Catalysts: Lessons from Photosynthesis*," *Acc. Chem. Res.*, 2009, 42, 1935-1943.
- Brimblecombe, R., et al., "*Solar Driven Water Oxidation by a Bioinspired Manganese Molecular Catalyst*," *J. Am. Chem. Soc.*, 2010, 132, 2892-2894.

Week 9
Carbon-dioxide fixation
Dark photosynthetic cycle
Artificial carbon-dioxide reduction: advances and challenges

Reading:
- Grills, D. C.; Fujita, E., "*New Directions for the Photocatalytic Reduction of CO2: Supramolecular, scCO2 or Biphasic Ionic Liquid-scCO2 Systems*," *J. Phys. Chem. Lett.*, 2010, 1, 2709-2718.
- Berg, J. M.; Tymoczko, J. L.; Stryer, L. in "*Biochemistry*," sections on Calvin cycle.

Week 10
Self-repairing and self-healing
Difference between living systems and engineered devices
Damage prevention vs. damage management

- Straight, S. D.; Kodis, G.; Terazono, Y.; Hambourger, M.; Moore, T. A.; Moore, A. L.; Gust, D., "*Self-Regulation of Photoinduced Electron Transfer by a Molecular Nonlinear Transducer*," *Nature Nanotechnology*, 2008, 3, 280-283.
- Ivanov, A. G.; Sane, P. V.; Hurry, V.; Oquist, G.; Huner, N. P. A., "*Photosystem II Reaction Centre Quenching: Mechanisms and Physiological Role*," *Photosynth. Res.*, 2008, 98, 565-574.
- Trask, R. S.; Williams, H. R.; Bond, I. P., "*Self-Healing Polymer Composites: Mimicking Nature to Enhance Performance*," *Bioinspiration Biomimetics*, 2007, 2, P1-P9.