Photoelectrochemical Polymerization of Pyrrole by Photosystem I

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ViNSE

Photosystem I (PSI)

- Protein in photosynthesizing organisms
- Inexpensive and easy to extract
- Robust Redox capabilities
- Two reaction centers
  - Iron-Sulfur (F_B)
  - Chlorophyll pair (P_{700})

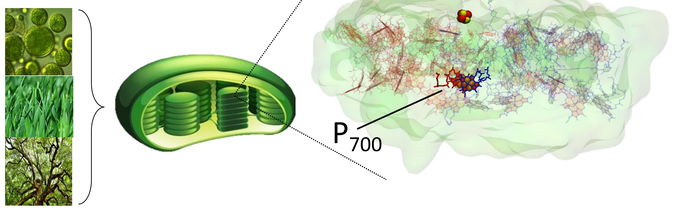
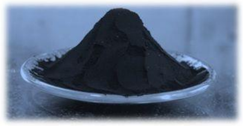


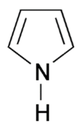
Figure 1: (Left) Plant cells. (Middle) Chloroplast organelles. (Right) PSI protein

Polypyrrole

Conducting Polymer
- High conductivity >100 S/cm
- Stability in oxidized state
- Relatively low onset potential
- Biocompatibility
- Ease of synthesis

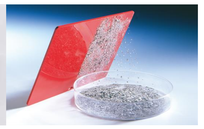


Polypyrrole Powder



Pyrrole Monomer

Electromagnetic Shielding

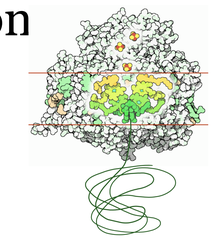


Anti-electrostatic Coating

Product Applications
- Polypyrrole-coated stretchable textile
  - Anti-electrostatic coating
  - Electromagnetic shielding

Photoelectrochemical Polymerization

- Sunlight powers PSI Redox reactions
- PSI redox reactions grow polymer chain
  - Oxidation occurs at P_{700}
- Oxidative radical polymerization



Polypyrrole-Protein Conjugate

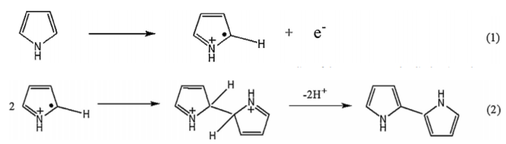


Figure 2: The free radical polymerization mechanism of Polypyrrole. (1) initiation step, formation of radical cation. (2) Coupling of radical cations and deprotonation to form bipyrrole. Image credit *Synthetic Metals*. 2013, 175, 183-191

Infrared Spectroscopy Proof

- IR spectroscopy – view the fingerprint of components
- Both components are present in our reaction product
- Subtracted solid lines in (right) have the same peaks as the dotted lines
  - Both components present

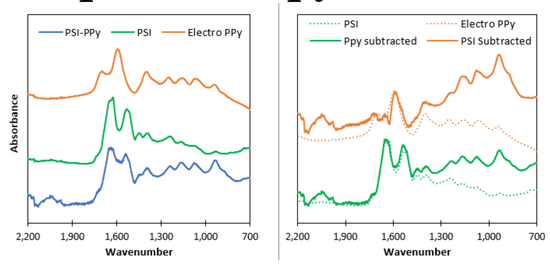


Figure 3: (Left) Pure component and reaction product IR spectra. (Right) Subtracted IR spectra comparisons. Image credit Joshua Passantino

SDS-PAGE to Detect Attachment

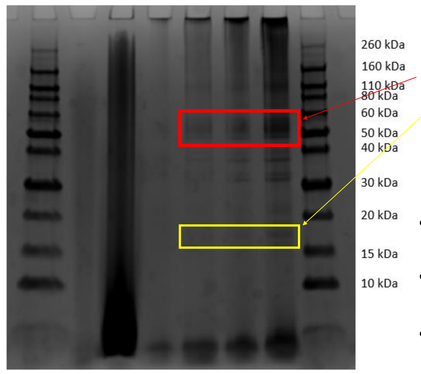
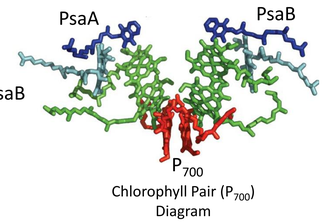


Figure 4: SDS-PAGE of PSI. Image credit Joshua Passantino



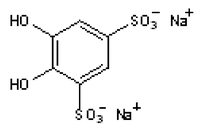
Chlorophyll Pair (P_{700}) Diagram

- Separate subunits by mass
  - Higher weight is at the top
- Prove Polypyrrole is attached at the P_{700} site
- P_{700} consists of PsaA and PsaB subunits
  - PsaA/PsaB site expected to shift upward to a higher weight value

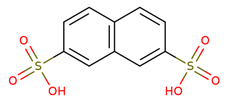
Dopants

Used to enhance polymerization process, conductivity of polymer, and modulate product structure

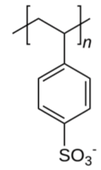
- Tiron
  - Anionic, higher charge to mass ratio



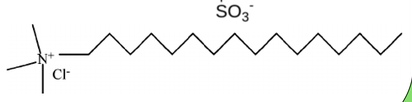
- Naphthalenedisulfonic Acid
  - Anionic, encourages anisotropic polymer structure



- Polystyrene sulfonate (PSS)
  - Anionic, helps grow long polymer chains, renders soluble product



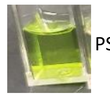
- Cetyltrimethylammonium Chloride
  - Cationic, similar dopant known to encourage nanofiber structures



Visible Polypyrrole Growth

Growing Polypyrrole will qualitatively change the color
- Light green – Photosystem I protein soluble in solution
- Dark Green – Growth of Polypyrrole

- Light dependent Photosystem I reaction
- PSS can auto-polymerize pyrrole, however PSI directs the polymerization



PSI

PSI Py

PSS Py

PSI PSS Py

Picture showing vials before and after illumination for 190 min. Image credit Joshua Passantino

Absorption Spectra Results
- The Polypyrrole absorbance peak (750-1000 nm) is increasing = polymerization of pyrrole
- The PSI peak (650-700 nm) is decreasing = possible chlorophyll damage

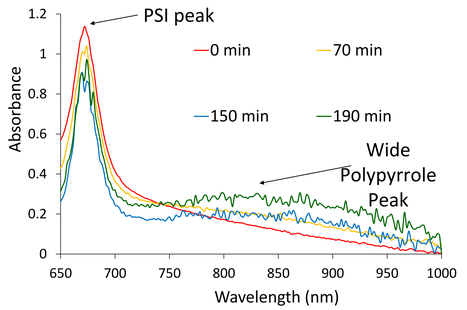


Figure 5: Normalized Absorption Spectra of PSI PSS (at 1 unit per volume), and Polypyrrole

Next Steps: Characterization

- Important factor: Solubility
  - Good solubility = uniform film = facile characterization
  - PSS produced most soluble products, therefore the most uniform films
- Raman Spectroscopy
  - Surface Enhanced Raman Spectroscopy – most sensitive, detect low concentrations of analyte
  - Confocal Raman Spectroscopy – highest spatial resolution, ability to analyze in 3 dimensions
- Conductivity measurements using four-point probe
- Photoactivity measurements

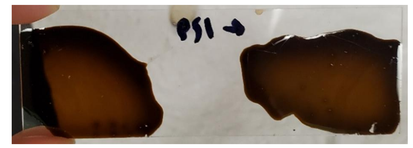
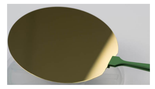


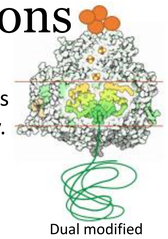
Image showing the uniform films produced from drop casting PSS enhanced solution. Image credit Joshua Passantino



(Left) Gold coated silicon wafer. (Right) Thermo Scientific DXR Raman microscope

Conclusions/Future Directions

- The Photosystem I protein can polymerize pyrrole!
- Polystyrene Sulfonate enhances that polymerization and produces soluble reaction product ideal for uniform films and photoactivity.
- Future Directions
  - Dual modification – reduced metal at F_B site
  - Analyze stability
  - Make photovoltaic device



Dual modified Photosystem I protein

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