Capture and conversion of solar energy via phototrophy into fermentable sugars producing alcohols and alkanes is a primary focus of sustainable fuel advocates. However, many inefficiencies associated with a multitude of process steps make this economically marginal in most locations. These, combined with concerns of large scale monoculture farming, food versus fuel debates, fresh water limitations, and poor productivity have limited global biofuel implementation. Recently the potential for hybrid solar capture and conversion platforms based on photovoltaics with transformation via a combination of electro- and bio-chemical processes was recognized. A basic example is water hydrolysis using photovoltaic energy yielding H2 for consumption by chemoautotrophs producing biofuels. These systems offer significant advantages and can sustainably produce diverse chemicals and fuels. However, H2 chemoautotrophy is not ideal for infinitely scalable processes. Our research focuses on coupling alternative chemoautotrophic processes to photovoltaics for energy storage and interconversion. We study inorganic chemicals that redox cycle electrochemically and are utilized as microbial energy and reducing equivalent sources. These studies lead to mechanistic understanding of novel microbial electron transport systems and their application. As part of this we recently identified a novel chemolithotrophic mechanism of dissimilatory phosphite oxidation (DPO) coupled to CO2 autotrophy via a new natural carbon fixation pathway. Our studies reveal that DPO is far more prevalent than previously assumed and highlights the likelihood that reduced phosphorous compounds are important constituents of phosphorous geochemistry. These studies represent an exciting new direction for energy transformation and sustainable commodity chemical production at a time of global bioavailable phosphorouslimitation, and the increasing necessity for novel CO2 sinks.