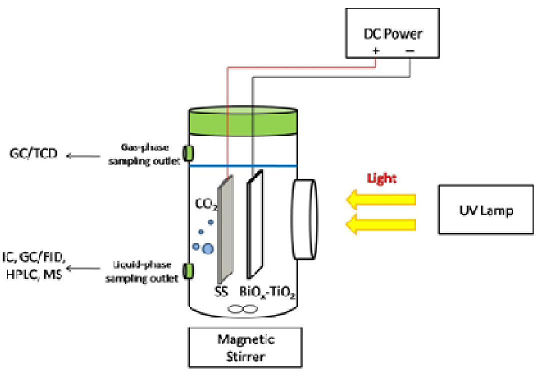
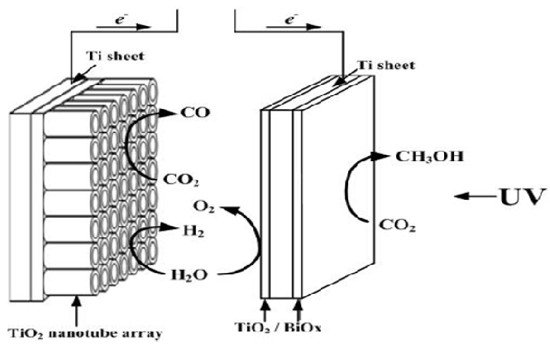
ARTIFICIAL PHOTOSYNTHESIS VIA PHOTOELECTROCHEMICAL AND PHOTOCATALYTIC REDUCTION OF CO_2 WITH THE SIMULTANEOUS PRODUCTION OF H_2

Michael R. Hoffmann
James Irvine Professor of Environmental Science
W. M. Keck Laboratories, California Institute of Technology, Pasadena, CA, USA

Over the past decade, there has been a renaissance of interest in the artificial photo-fixation of carbon dioxide due to concerns about global warming and the renewed interest in the development of over non-fossil fuel sources of energy. Thus, there has been a resurgence of research into electrochemical and photochemical CO_2 fixation and conversion into energy rich products. Simple metal electrodes including copper and zinc have been employed for the electrochemical CO_2 reduction. In addition, semiconductor electrodes based on CdS, GaP, InP and GaAs and many others have been used for the photo-electrochemical reduction of CO_2. In our lab, we have explored several different electrode and photocatalyst combinations that could be used and readily prepared on a large-scale at relatively low cost. In one approach, a photo-electrochemical cell, which consists of anodes prepared on Ti metal base supports, is prepared by coating successive layers of various mixed-metal, semiconducting oxides onto the Ti base with the top layer consisting of Bi-doped TiO_2 and coupled with either naked metal cathodes or various semiconductor-coated metal counter-electrodes. In another approach, we have explored the use of functionalized TiO_2 nanotube arrays synthesized directly on to Ti-base metal electrodes. These two different electrode configurations are illustrated below:





We have observed that depending on the specific solution-phase or electrolytic conditions that CO_2 is reduced to CO, HCOOH, HCHO, CH_3OH and CH_4 either electrochemically or photocatalytically using CdS quantum-dot coated TiO_2 as a base support. We also have isotopic-labeling evidence of the conversion of CO_2 to higher molecular weight hydrocarbons via a photocatalytic Fischer-Tropsch reaction involving CO. At the same time there is a competition for electrons by protons and water resulting in the simultaneous formation of H_2.

$$CO_2 + 2\,H^+ + 2e^- \rightarrow CO + H_2O$$

$$CO_2 + 2\,H^+ + 2e^- \rightarrow HCOOH$$

$$CO_2 + 4\,H^+ + 4e^- \rightarrow HCHO + H_2O$$

$$CO_2 + 6\,H^+ + 6e^- \rightarrow CH_3OH + H_2O$$

$$CO_2 + 8\,H^+ + 8e^- \rightarrow CH_4 + 2\,H_2O$$

$$(2n + 1)\,H_2 + n\,CO \rightarrow C_nH_{(2n+2)} + n\,H_2O$$