

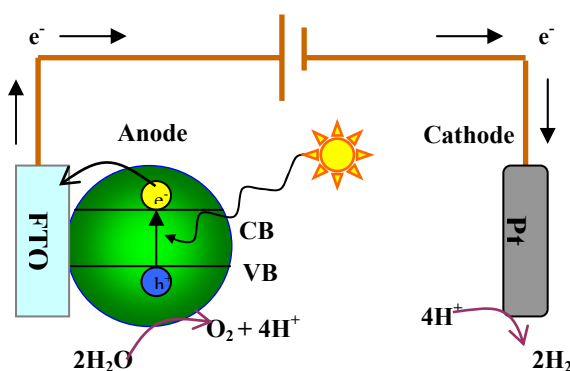
# Solar Hydrogen Conversion and Visible-Light Photocatalysis

## Background:

The photoelectrochemical production of hydrogen has drawn considerable attention due to the importance of using hydrogen as a clean and renewable source. Photoelectrochemical systems can produce H<sub>2</sub> from water using special semiconductor materials and energy from sunlight. Wide band-gap semiconductors, such as TiO<sub>2</sub>, are the most promising materials in the field of solar hydrogen conversion. Water splitting in a photoelectrochemical cell is the result of two processes. First, photons are absorbed by the semiconductor and generate electron-hole pairs. When n-TiO<sub>2</sub> is exposed to light and the energy exceeds the band gap, electrons (e<sup>-</sup>) and holes (h<sup>+</sup>) are formed according to the following process:



In the second process the holes reaching the surface react with electrons transferred from reducing species in the electrolyte. Gaseous oxygen formation occurs at the TiO<sub>2</sub> photoelectrode and hydrogen at the cathode when the electrons pass through the external circuit (Figure 1). The global reaction is:



**Figure 1:** Photoelectrochemical setup to evaluate solar hydrogen conversion

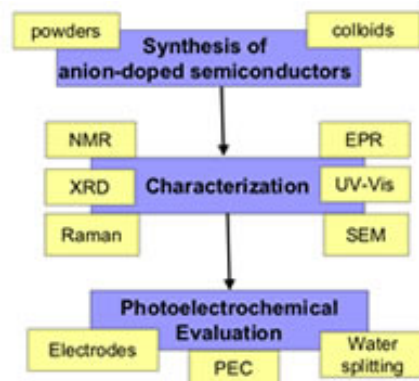
Wide band-gap semiconductors, such as TiO<sub>2</sub>, are the most promising materials in the field of solar hydrogen conversion due to their good stability and catalytic activity, but their poor visible light absorption represents a major problem. The discovery of new, more efficient photocatalysts for water splitting is still very challenging.

## Research Overview:

The band-gap modification of the wide band-gap semiconductors has been our fundamental goal in order to improve their efficiency and applicability. Modifying the band structure to reduce the band gap has been attempted in the past by doping with a variety of transition metals such as vanadium (TM-TiO<sub>2</sub>). Our previous <sup>13</sup>C solid-state NMR studies demonstrated that a vanadium-doped, supported TiO<sub>2</sub> photocatalyst is quite active using visible (396-450 nm) light for the oxidation of ethanol [1]. Although the TM-TiO<sub>2</sub> material may effectively absorb visible light, as recently shown, their use in electrodes largely indicates that the photocurrent generated in thin films, irrespective of the metal ion used to date, is not improved.

One promising approach is to synthesize a reduced form of TiO<sub>2</sub> by substituting anions (main group elements such as C, S, B and N) for oxygen in the titania lattice or be present in interstitial sites [2]. Our research consists of three phases (Figure 2):

- **Synthesis** of new materials
- **Characterization** of their structural and physical properties in order to optimize their performance.
- **Evaluation** for water splitting



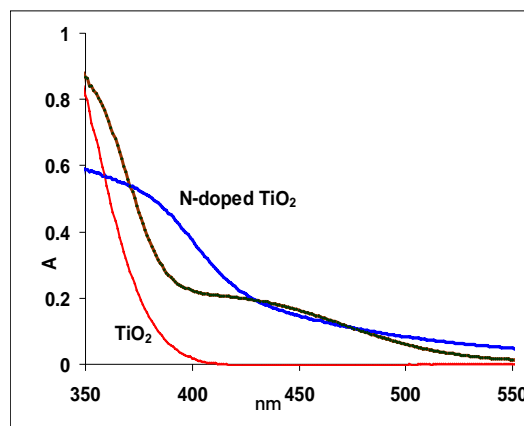
**Figure 2:** Schematic approach for the synthesis, characterization and evaluation of the photoactive materials.

In order to develop better materials for solar energy applications, in-depth photoelectrochemical and spectroscopic characterization of anion-doped metal oxide materials are conducted. Analytical methods employed to characterize these materials include electron paramagnetic resonance (EPR), UV-vis spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), elemental analysis and X-ray photoelectron (XPS). In particular, our lab specializes in characterizing dopant species using solid-state NMR. The photoactivity of the electrodes was evaluated using a 3-electrode configuration quartz photoelectrochemical cell (PEC) using simulated solar irradiance.

## Some Results:

### UV-Visible Spectroscopy

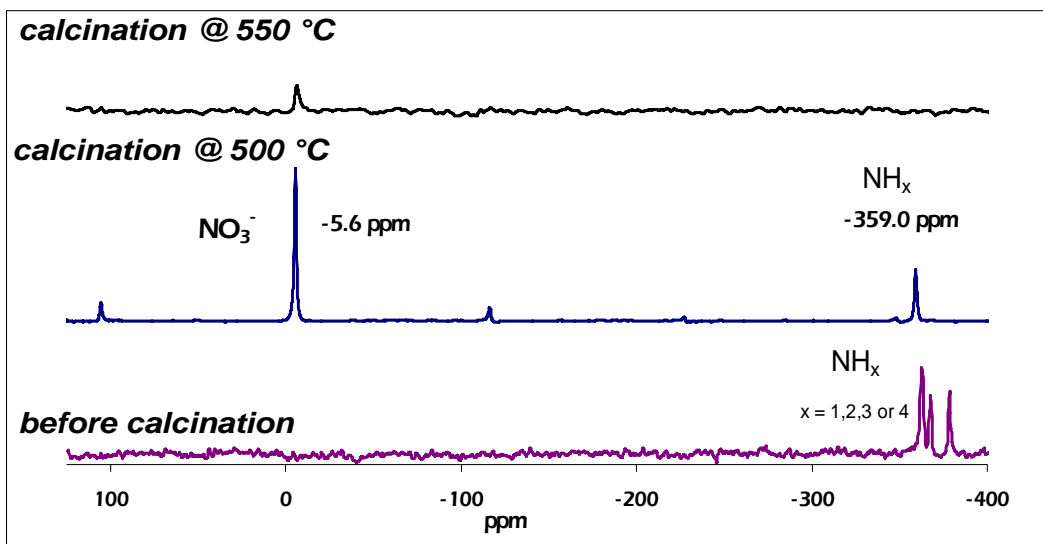
The anion doping approach produces materials that are not hampered by fast  $e^-/h^+$  recombination to the same extent as TM-TiO<sub>2</sub> materials, while the optical absorption is red-shifted somewhat into the visible range. UV-vis spectra show that anion doping extends the visible absorption of TiO<sub>2</sub> from the UV region ( $\lambda < 380$  nm) out to 500 nm (Figure 3) [3].



**Figure 3:** The electronic absorption spectra of the doped nanoparticles clearly show an absorption maximum centered at 435 nm and their absorption onset is ~550 nm.

### Solid-State NMR and EPR

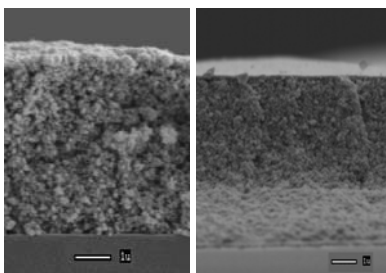
SSNMR experiments indicate that the doping species' chemical state is highly oxidized: <sup>15</sup>N cross-polarization magic angle spinning (MAS) shows that nitrogen is present as nitrate (NO<sub>3</sub><sup>-</sup>,  $\delta_{iso} = -5.6$  ppm) (Figure 4). EPR results indicate that paramagnetic species are not just the result of vacancies and defects but rather a unique paramagnetic center as the previously reported NO species in N-doped TiO<sub>2</sub>.



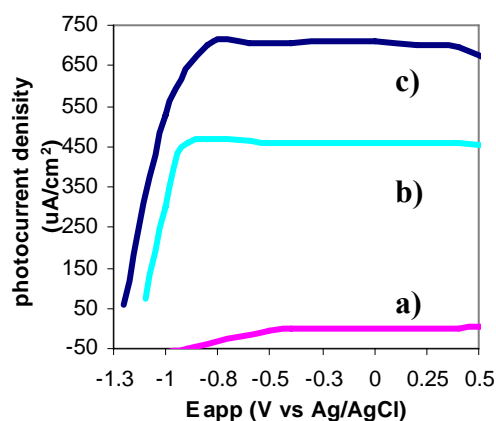
**Figure 4:**  $^{15}\text{N}$  cross-polarization magic angle spinning (MAS) before calcination shows that nitrogen is present as three types of amines identified as  $\text{NH}$ ,  $\text{NH}_2$  and  $\text{NH}_4^+$ . After calcination these species are oxidized to  $\text{NO}_3^-$ , along with residual  $\text{NH}_x$  species due to incomplete oxidation. The direct polarization (DP) experiment indicates complete oxidation after treatment at  $550\text{ }^\circ\text{C}$  [3].

## Photocatalytic and Photoelectrochemical Evaluation

The reduced forms of N-doped, S-doped and B-doped  $\text{TiO}_2$  powders are photocatalytically active under visible illumination as shown by the photochemical oxidation of organic compounds. In addition, thin film electrodes were prepared from the powders and colloidal materials (Figure 5). The anion-doped  $\text{TiO}_2$  colloidal electrodes increased the photocurrent densities of  $\text{TiO}_2$  under simulated solar light (Figure 6) [2].



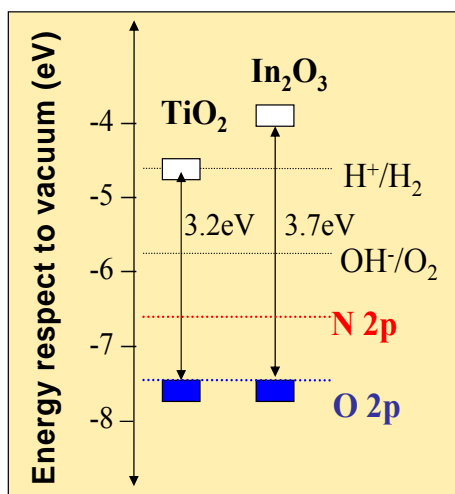
**Figure 5:** SEM cross-sectional images of 2 layer  $\text{TiO}_2$  films: (left) powder P25 and (right) colloidal anion-doped  $\text{TiO}_2$ .



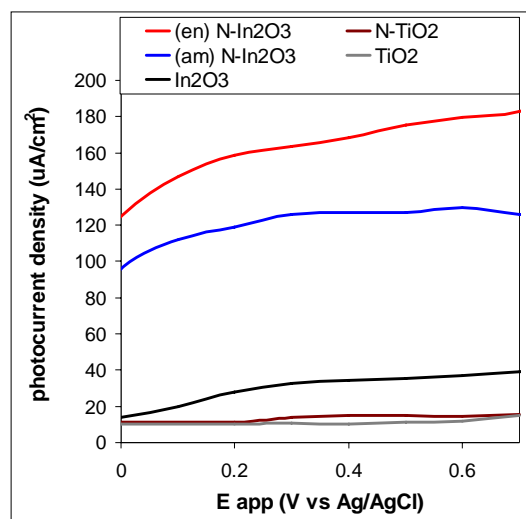
**Figure 6:** Photocurrent density as a function of the applied voltage ( $E_{\text{app}}$ ): a) dark current, b) n- $\text{TiO}_2$  colloid, and c) (TBN) C,N-doped  $\text{TiO}_2$  electrode in KOH and methanol.

## Development of New Materials

We recently reported work on a new visible-light absorbing photocatalyst, N-doped  $\text{In}_2\text{O}_3$ , which shows promise as an efficient material [4]. N-doped  $\text{In}_2\text{O}_3$  material reduces band gap, and we observe that N can either substitute for oxygen in the lattice or be present in interstitial sites. N-doped  $\text{In}_2\text{O}_3$  has a higher photoactivity for water splitting than N-doped  $\text{TiO}_2$ , even though its initial band-gap is larger (3.5 eV) (Figure 7). The photocurrent densities of N-doped  $\text{In}_2\text{O}_3$  electrodes are at least double those of undoped  $\text{In}_2\text{O}_3$  and approximated 50 times better than N-doped  $\text{TiO}_2$  under visible irradiation, and without sacrificial reagents (Figure 8).



**Figure 7:** Energy positions of conduction and valence band edges (white and blue rectangles, respectively) for  $\text{TiO}_2$  and  $\text{In}_2\text{O}_3$ .



**Figure 8:** Photoelectrochemical evaluation of N-doped  $\text{TiO}_2$  and  $\text{In}_2\text{O}_3$  electrodes under UV-Visible light.

The results of NMR, EPR, XRD and XPS analysis provide very useful information towards understanding the structure of these new materials. This structural information will be used as a guide towards developing more efficient materials. Our current efforts are focused on developing new materials based on novel dopant-host systems [5] that we evaluate using the methods described above to improve the performance of these materials and to build structure-activity models for further improvements.

## Publications:

- 1) S. Klosek and D. Raftery, "Visible Light Driven V-Doped  $\text{TiO}_2$  Photocatalyst and its Photooxidation of Ethanol," *J Phys. Chem. B* **105**, 2815 (2001).
- 2) K. Reyes, E. Reyes and D. Raftery, "Photoelectrochemical Analysis of Anion-Doped  $\text{TiO}_2$  Colloidal and Powder Thin-Film Electrodes," *J. Electrochem. Soc.* **153**(7), A1296-A1301.

- 3) E. A. Reyes-Garcia, Y. Sun, K. R. Reyes-Gil and D. Raftery, " **$^{15}\text{N}$  Solid State NMR and EPR Characterization of N-Doped  $\text{TiO}_2$  Photocatalysts,**" *J. Phys. Chem. C.*, **111**(6), 2738-2748 (2007).
- 4) K. R. Reyes-Gil, E. A. Reyes-García and D. Raftery, "**Nitrogen-Doped  $\text{In}_2\text{O}_3$  Thin Film Electrodes for Photocatalytic Water Splitting,**" *J. Phys. Chem. C.*, accepted.
- 5) E. A. Reyes-Garcia, Y. Sun and D. Raftery, "**Solid State Characterization of the Nuclear and Electronic Environment of Boron and Fluoride Co-doped  $\text{TiO}_2$  Visible-light Photocatalysts,**" *J. Phys. Chem. C*, accepted.