Chapter 1

Introduction

Semiconductor photocatalysis has many potential applications for environmental problems.¹ One of the most-studied semiconductors has been TiO₂, as it has the advantage of being cheap, nontoxic, and stable. Studies on the surface chemistry of TiO₂ help answer important questions such as the active species for photooxidation, the fate of charge carriers, and the mechanism for transfer of charge to species bound to the surface.² Chapter 2 builds on our previous work monitoring surface species and surface traps on TiO₂ powders.³⁻⁵ FTIR spectroscopy is a powerful tool that can identify distinct molecular species assigned to trapped holes and electrons, as well as identify macroscale features such as free conduction band electrons. The absorption and oxidation of two organic molecules (decane and methanol) over TiO₂ surfaces were studied to gain insight into the gas phase and surface bound photooxidation products.

Our interests then turned towards visible light photocatalysis, as the potential to harvest the sun's energy to do useful chemistry is quite appealing. Chapter 3 outlines work on doping TiO_2 with nitrogen atoms in order to lower the bandgap energy into the visible region. Nitrogen doping proved to be a limited success, as a trade-off between visible and UV light activity was observed. The recent literature has shown a mix of successful and unsuccessful results^{6,7} after the initially reported success of nitrogen-doped TiO₂.⁸

Continuing the work on visible light photocatalysis, we moved into the field of photocatalytic hydrogen production from water. We have achieved successful production of hydrogen by attaching CdS and Ni to metal oxide supports such as microporous and mesoporous silicas (chapter 4) and niobium oxides (chapter 5). Characterization of these materials was performed using various analytical techniques to look at the chemical environment and fate of the nanosize CdS particles that had been introduced into these metal oxides of different shapes and sizes. Experimental conditions were then varied in order to achieve the highest rate of hydrogen production.

References

(1) Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.

(2) Thompson, T. L.; Yates, J. T. *Chem. Rev.* **2006**, *106*, 4428.

(3) Szczepankiewicz, S. H.; Colussi, A. J.; Hoffmann, M. R. J. Phys. Chem. B **2000**, *104*, 9842.

(4) Szczepankiewicz, S. H.; Moss, J. A.; Hoffmann, M. R. *J. Phys. Chem. B* **2002**, *106*, 7654.

(5) Szczepankiewicz, S. H.; Moss, J. A.; Hoffmann, M. R. J. Phys. Chem. B2002, 106, 2922.

(6) Livraghi, S.; Paganini, M. C.; Giamello, E.; Selloni, A.; Di Valentin, C.;Pacchioni, G. J. Am. Chem. Soc. 2006, 128, 15666.

(7) Batzill, M.; Morales, E. H.; Diebold, U. Phys. Rev. Lett. 2006, 96, 026103.

(8) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. Science 2001, 293,

269.