

## Effect of Fluorine on the Photocatalytic Properties of Titania

Jonathan I. Brauer, Gregory J. Szulczewski

Nitrogen and nitrogen/fluorine co-doped  $\text{TiO}_2$  nanoparticles, denoted as  $\text{N-TiO}_2$  and  $\text{N,F-TiO}_2$ , respectively, have been synthesized by a room temperature sol-gel method. The as-synthesized photocatalysts were characterized by BET isotherms, powder x-ray diffraction, x-ray photoelectron spectroscopy, as well as Raman, visible/IR diffuse reflectance spectroscopy. The unannealed material is the anatase phase, but largely amorphous with a surface area of  $\sim 80\text{m}^2/\text{gram}$ . The photoactivity of the photocatalysts was assessed by measuring the degradation of the methylene blue with visible light greater than 420 nm. The kinetics of methylene blue photodegradation was monitored by UV-vis spectroscopy and the reaction products were identified electrospray ionization mass spectrometry. The pseudo first order rate constant for methylene blue decomposition is larger with the  $\text{N,F-TiO}_2$  photocatalyst compared to  $\text{N-TiO}_2$ . The mechanism for methylene blue decomposition was characterized by monitoring the photodegradation products with mass spectrometry. For both the  $\text{N-TiO}_2$  and  $\text{N,F-TiO}_2$  photocatalysts we find that decomposition mechanism is photooxidation by hydroxyl radicals formed by hole mediated water splitting, rather than reduction by demethylation. We surmise that the fluorine dopants increases the oxidizing potential of the photogenerated holes in valence band, which lowers the barrier to create OH radicals and leads to the observed increase in the methylene blue decomposition rate.