

APPLICATIONS OF SEMICONDUCTOR PHOTOCATALYSIS FOR BOTH  
DEGRADATION OF ORGANICS AND HYDROGEN PRODUCTION

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## ABSTRACT

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to study illuminated  $\text{TiO}_2$  surfaces under both vacuum conditions and in the presence of organic molecules (decane and methanol). In the presence of a hole scavenger, electrons are trapped at Ti(III)-OH sites, and a free electrons are generated. These free electrons are seen to decay by either exposure to oxygen or to heat; in the case of heating, reinjection of holes into the lattice by loss of sorbed hole scavenger leads to a decrease in Ti(III)-OH centers. Decane adsorption experiments lend support to the theory that removal of hydrocarbon contaminants is responsible for superhydrophilic  $\text{TiO}_2$  surfaces. Oxidation of methanol led to formation of surface bound formic acid.

Titanium dioxide was then doped with nitrogen atoms via high temperature treatment with ammonia, toward the goal of developing a catalyst capable of using visible light to degrade organic substrates. Catalyst efficiency was tested by monitoring formate degradation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  under visible light using ion chromatography. However, reduced photocatalytic activity in the UV region, as well as a strong synthesis temperature dependence on catalytic efficiency, was observed. The N-doped  $\text{TiO}_2$  surface was probed with diffuse infrared Fourier transform spectroscopy (DRIFTS), leading us to conclude that Ti-N triple bond defect sites control visible light activity and lead to an apparent reduction in overall crystallinity.

Visible light photocatalytic  $\text{H}_2$  production was then studied. Microporous and mesoporous silicas (Zeolite-Y, Zeolite-L, SBA-15) and niobium oxides ( $\text{KNbO}_3$ ,  $\text{K}_4\text{Nb}_6\text{O}_{17}$ ) were combined with nanoparticulate CdS particles and Ni to form hybrid photocatalysts that produced  $\text{H}_2$  from water/ethanol solutions under visible light

irradiation. Silica cavity size, which determines CdS particle size, and photocatalytic activity were found to be correlated. Photocatalytic activity was seen to decrease under acidic or basic conditions with an associated negative ionic strength effect. In the niobate catalysts, Ni doping was shown to lead to higher-energy Nb-O bonding states and to compete with Cd for ion exchange sites. XPS analysis indicated loss of Cd<sup>2+</sup> ion from the metal oxide supports occurred during the course of the photochemical reaction, with apparent retention of bound CdS for most catalysts.

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