

While TiO_2 , on which most of the photocatalytic studies have focused, shows a relatively high reactivity and chemical stability under ultraviolet (UV) light (larger than the band gap of 3.2 eV in the anatase crystalline phase or the wavelength $\lambda < 387$ nm), the development of photocatalysts that can yield high reactivity under visible light ($\lambda > 380$ nm) has been desired to make use of the main part of the solar spectrum, and to extend their applications to living spaces with relatively poor interior lighting illumination. Here we present a novel photocatalyst, N-doped TiO_2 , showing a significant improvement over TiO_2 in photocatalytic activity under visible light.

$\text{TiO}_{2-x}\text{N}_x$ films, which were prepared by sputtering the TiO_2 target in an N_2 (40%)/Ar gas mixture followed by annealing at 550°C in N_2 gas, noticeably absorbed visible light at less than 500 nm, whereas the TiO_2 films do not. The films are crystalline with features assignable to a mixed structure of the anatase and rutile crystalline phases, as determined by X-ray diffraction (XRD). Photocatalytic activity has been evaluated by measuring the decomposition rates of methylene blue adsorbed on the film surface as a function of the cutoff wavelength of the optical high-path filters under fluorescent light irradiation (Fig. 1). As a result, significant photocatalytic activity under 500 nm has been observed in the $\text{TiO}_{2-x}\text{N}_x$

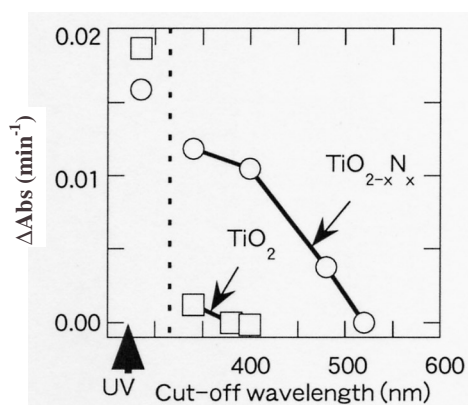


Fig. 1 Photocatalytic decomposition rates (measuring the change in absorption of the reference light) of methylene blue as a function of the cutoff wavelength of the optical high-path filters under fluorescent light (1W), compared with the results under black light (BL, 1W) illumination.

film. CO_2 evolution during the photooxidation of gaseous acetaldehyde in the anatase $\text{TiO}_{2-x}\text{N}_x$ powder samples, prepared by annealing TiO_2 in an NH_3 +Ar gas flow, has also been evaluated (Fig. 2). The rate for $\text{TiO}_{2-x}\text{N}_x$ is more than five times higher than that for TiO_2 in the visible range of $\lambda \geq 400$ nm. These results clearly show that the photocatalytic activity of the $\text{TiO}_{2-x}\text{N}_x$ samples are superior to that of the TiO_2 samples in the visible range of irradiation, while both samples yield similar activity in the UV range of irradiation.

We have also calculated densities of states for the doping of N in the anatase TiO_2 crystal, by the full-potential linearized augmented plane wave formalism in the framework of the local density approximation. As a result, the substitutional doping of N for O has proven effective for the band-gap narrowing and the visible-light photocatalytic activity as N 2p states mix with O 2p states in the valence bands. On the other hand, molecularly chemisorbed states along with the interstitial doping of N are too deep in the band gap to amalgamate with the band states of TiO_2 , and are thus unlikely effective for photocatalysis. These insights are indeed consistent with the experimental results including X-ray photoemission spectroscopy studies, where the peak assigned to be a Ti-N formation is indispensable for the visible-light photocatalysis. (Report received on July 2, 2001)

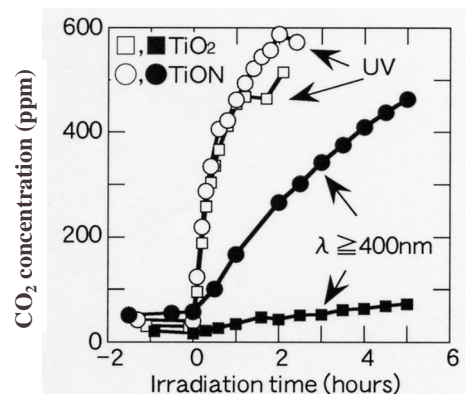


Fig. 2 CO_2 evolution as a function of irradiation time (light-on at zero) during the photooxidation of acetaldehyde gas (with an initial concentration of 485 ppm in 1 liter bottle) under UV irradiation (BL, 10W) and visible irradiation ($\lambda \geq 400$ nm, fluorescent light (10Wx2) cut by the optical high-path filter).