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Enhanced Nitrogen Doping in TiO_2 Nanoparticles

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ABSTRACT

$TiO_{2-x}N_x$ nanoparticles were prepared by employing the direct amination of 6–10-nm-sized titania particles. Doping on the nanometer scale led to an enhanced nitrogen concentration of up to 8%, compared to ≤2% in thin films and micrometer-scale TiO_2 powders. The synthesized $TiO_{2-x}N_x$ nanocrystals are catalytically active and absorb well into the visible region up to 600 nm, thus exemplifying the use of a nanostructure-based synthesis as a means of producing novel photocatalytic materials.

The efficient utilization of solar energy is one of the major goals of modern science and engineering that will have a great impact on technological applications.[1–5] Of the materials being developed for photocatalytic applications, titanium dioxide (TiO_2) remains the most promising because of its high efficiency, low cost, chemical inertness, and photostability.[6–10] However, the widespread technological use of TiO_2 is impaired by its wide band gap (3.2 eV), which requires ultraviolet irradiation for photocatalytic activation. Because UV light accounts for only a small fraction (8%) of the sun's energy compared to visible light (45%), any shift in the optical response of TiO_2 from the UV to the visible spectral range will have a profound positive effect on the photocatalytic efficiency of the material.[11] Here we report a simple nitrogen-doping method for nanometer-sized visible-light TiO_2 photocatalysts. The prepared photocatalysts show an enhancement in the photodegradation efficiency of methylene blue under visible light (wavelength ≥ 390 nm) irradiation compared to commercially available TiO_2 catalyst.

An initial approach to shifting the optical response of TiO_2 from the UV to the visible spectral range has been the doping of TiO_2 with transition-metal elements.[12–18] However, metal doping has several drawbacks. The doped materials have been shown to suffer from thermal instability, and the metal centers act as electron traps, which reduces the photocatalytic efficiency. Furthermore, the preparation of transition-metal-doped TiO_2 requires more expensive ion-implantation facilities.[19,20] Recently, it was shown that the desired band gap narrowing of TiO_2 can be better achieved by using anionic dopant species rather than metals ions.[11,21,22] Substitutional doping of nitrogen was found to be most effective because its p states contribute to the band gap narrowing by mixing with O 2p states. Recently, Asahi et al. showed that TiO_2 films can be doped with nitrogen by sputtering methods and exhibit thereafter enhanced photoactivity in the visible spectral range.[11] Considerable effort has been undertaken to dope TiO_2 thin films and powders with nitrogen by annealing TiO_2 at elevated temperature under NH_3 flow for several hours. Nevertheless, the doping process on these micrometer-sized TiO_2 systems resulted in only small amounts (≤2%) of nitrogen incorporation.[11]

We have developed an alternative nanoscale synthesis route that leads to increased nitrogen dopant concentration (up to 8%) in titania. $TiO_{2-x}N_x$ has been synthesized at room temperature by employing the direct amination of TiO_2 nanoparticles. The synthesized $TiO_{2-x}N_x$ nanoparticles are photocatalytically active, with absorbance that extends into the visible region up to 600 nm.

Small TiO_2 nanocrystals were prepared by the controlled hydrolysis of titanium (IV) isopropoxide in water under controlled pH.[23,24] By adjusting the pH of the solution, TiO_2 nanocrystals in the size range of 3 to 10 nm can be synthesized as transparent colloidal solutions, which are stable for extended periods.[24] To introduce the nitrogen dopant into the titania nanoparticles, triethylamine is added to the colloidal nanoparticle solution. The addition of amine to the nanoparticle solution results in the formation of yellow nanocrystals (mean diameter of ~10 nm).[23] X-ray powder diffractometry (XRD) and high-resolution transmission electron microscopy (HRTEM) demonstrate that the treated

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