

Semiconductor Metal Oxide Nanoparticles for Visible Light Photocatalysis

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TiO₂ is a promising photocatalyst for environmental remediation processes. TiO₂ nanoparticles offer additional advantages if the size can be optimized.(1) In bulk or large particles more than 90% of the photo-generated carriers recombine. (2-3) Therefore, decreasing the total volume of the particle decreases the recombination probability making available more carriers for the oxidation or reduction of a surface adsorbed pollutant. However, there is an optimal size. Small particles have large total surface area where the surface recombination can occur.(2-3) A size optimization is, therefore, required.

Additionally, the large band gap of TiO₂ nanoparticles has to be tailored in order to provide additional increment in the photocatalytic efficiency.(4-5) Nanoparticles, with their increased surface area, provide surface states within the bandgap to effectively reduce the band gap.(6) However, as discussed above, the particle size cannot be decreased below a critical limit. Another way of decreasing the effective band gap is by doping with appropriate dopant

This project includes synthesis, characterization, and application of TiO₂ nanoparticles as photocatalyst. Specifically, the multifold objectives of this proposal are:

□To synthesize TiO₂ nanoparticles with particle sizes ranging between 1 and 20 nm, and to reproducibly dope the nanoparticles with various dopants.

□To characterize the nanoparticles for structural, chemical and optoelectronic properties.

□To utilize first-principles calculations to acquire an atomistic understanding of nanoparticle properties.

□To develop an understanding of the chemical and photochemical properties of pure and modified TiO₂ nanoparticles.

1. Deposition temperature effect on nano-TiO₂ structure and size distribution.

Doped and undoped TiO₂ nanoparticles with narrow size distribution were deposited on stainless steel mesh substrates by metallorganic chemical vapor deposition.□The chemical composition of TiO₂ nanoparticles was measured by energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy.□X-ray diffraction and transmission electron microscopy were performed to investigate the size and the size distribution of particles as well as the structural phase transitions.□For pure TiO₂, the results showed that anatase polycrystalline nanoparticles with average size from 23 to 31 nm were obtained for substrate temperatures between 350 and 600 °C (Fig. 1).□Particles deposited below 350 °C were X-ray amorphous and rutile began to precipitate at temperature above 700 °C.□The particles synthesized at 600 °C had the smallest size and narrowest size distribution.

The growth of anatase particles was attributed to the competition between the effect of calcination and deposition rate. At low temperature, the effect of deposition rate dominated the anatase nucleation and growth process. The

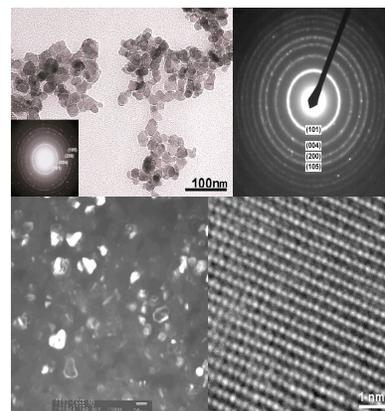


Fig. 1: TEM bright field image, diffraction pattern, dark field image and lattice image of TiO₂ nanoparticles.

change of TTIP concentration and residence time in the chamber and the increased nucleation density decreased the size of anatase nanoparticles with the increase in substrate temperature between 350 °C and 600 °C. At substrate temperatures above 600 °C, rutile started to form. Above the phase transition point, the growth process of anatase was dominated by the calcination effect from the substrate.

2. Effects of metal ion dopants on the photoreactivity of TiO₂ nanoparticles.

TiO₂ nanoparticles, with and without metal ion dopants, were synthesized using metallorganic chemical vapor deposition process. In order to improve the photocatalytic activity transition metal ions, including Pd²⁺, Pt⁴⁺, Nd³⁺ and Fe³⁺, were added to pure TiO₂ nanoparticles. The effects of dopants (~1%) on photocatalytic kinetics were investigated by the degradation of 2-chlorophenol under an ultraviolet light source. The results, presented in Fig. 2, showed that the TiO₂ nanoparticles with the transition metal dopants have higher photocatalytic activity than undoped TiO₂. Nd doping was most effective in the enhancement of the photoactivity of the TiO₂ nanoparticles. The 90% destruction time of 2-CP was reduced from 60 min for the undoped TiO₂ nanoparticles to 25 min for the 1 at.% Nd doped nano TiO₂. The apparent quantum yield was 2.5 times that of Degussa P25 and 3 times that of undoped TiO₂. □

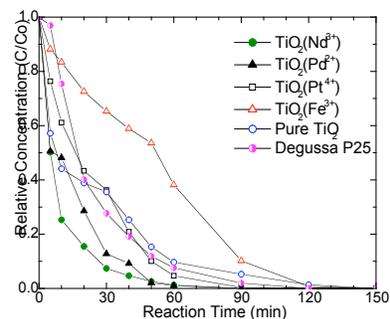


Fig. 2: Dopant effect on TiO₂ photactivity

The enhancement of the photocatalytic efficiency was related to the size differences between the host Ti⁴⁺ ionic radii and the dopant's ionic radii. Smaller ionic radii Fe³⁺ did not help the oxidation of 2-CP whereas all the larger ionic radii dopants did, particularly Nd³⁺. Fe, goes on the substitutional sites causing very little localized charging effects and oxygen vacancies which can trap electrons and increase the lifetime of holes. When Pd and Nd go on the substitutional sites, they can cause large the localized charging effects and generate more oxygen vacancies, which, in turn, increase the oxidation reaction rate.

3. Size dependence of structural, optical, and photocatalytic properties of TiO₂ nanoparticles.

Polycrystalline TiO₂ anatase nanoparticles with different average sizes (12, 17, 23 nm) were synthesized by metallorganic chemical vapor deposition. The particle sizes were determined by x-ray diffraction and transmission electron microscopy. The specific surface areas varied between 65 and 125 m²/gm, as measured by Brunauer-Emmett-Teller method. The size effects on the thermodynamic stability of TiO₂ were analyzed by annealing samples in the temperature range of 700 to 800 °C. Only anatase to rutile phase transformation occurred. The transformation rate was accelerated with the decrease of initial particle size (Fig.3). The activation energy was calculated from the XRD data. The activation energy decreased from 298.85 to 180.28 kJ/mol as the initial anatase particle size decreased from 23 to 12 nm. Photoabsorption

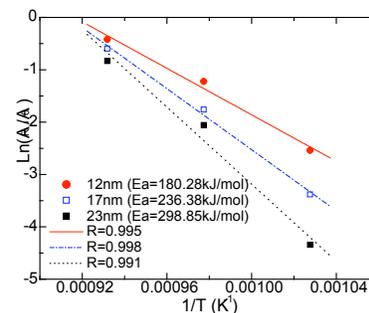


Fig. 3: Effect of particle size on Activation energy for anatase-rutile phase

measurements showed a red shift of the absorption edges with the decrease in the particle size down to 17 nm. Below this particle size, a blue shift was observed. Photodegradation of 2-chlorophenol solutions under ultraviolet irradiation showed 17 nm sample had the highest photoreactivity.

Smaller TiO₂ nanoparticles have lower activation energy and it is easier to overcome the energy barrier to new phase. The optimal size for photoreactivity is determined by several aspects of TiO₂ including surface area, light absorption efficiency, and charge carrier recombination rate.

4. Nd³⁺ doped TiO₂ nanoparticles for band gap narrowing.

Undoped and Nd³⁺ (0.6, 1, 1.5 at. %) -doped TiO₂ nanoparticles were synthesized by metallorganic chemical vapor deposition in order to tailor the band gap of TiO₂. The structure of the samples was analyzed by x-ray diffraction and transmission electron microscopy. The results showed that the nanoparticles have a polycrystalline anatase structure with a grain size of 20 - 23-nm for both doped and undoped TiO₂ samples. There is a very small reduction of the average particle size for Nd-doped TiO₂. The doping reduced the band gap. The band gap was measured by ultraviolet-visible light absorption experiments and by near-edge x-ray absorption fine structure. With increased dopant concentration, the absorption edge shifted to a longer wavelength and TiO₂:1.5% Nd had the largest red shift, ~ 0.55 eV. The maximum band gap reduction was 0.55 eV for 1.5 at% Nd-doped TiO₂ nanoparticles. Density functional theory calculations using the generalized gradient approximation with the linearized augmented plane wave method were used to interpret the band gap narrowing.

The band gap narrowing was primarily attributed to the substitutional Nd³⁺ ions. Some electronic states are introduced into the band gap of TiO₂ by Nd 4*f* electrons, which are located close to the lower edge of the conduction band to form the new lowest unoccupied molecular orbital. Consequently, the absorption edge transition for the doped material can be from O 2*p* to Nd 4*f* instead of Ti 3*d*, as in pure TiO₂. The theoretical calculations support the existence of substitutional Nd ions in the TiO₂ lattice.

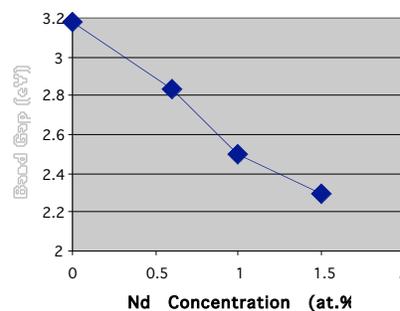


Fig.4: Bandgap variation with Nd doping.

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