

A correlation between activation energy and light absorption of WO₃ incorporated TiO₂

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Abstract

The variation of electrical conductivity properties and light absorption properties are studied in W⁶⁺ incorporated TiO₂. Both conductivity and light absorption depend on the percentage of W⁶⁺ incorporated into the crystal matrix of TiO₂. The activation energy decreased by a maximum of 30% as a result of doping and the lowest activation energy was measured when the dopant concentration was 0.2%. The light reflectance decreased with the dopant percentage, but not in a monotonically decreasing fashion. The variation of light reflectance as a function of dopant concentration showed a minimum when the dopant concentration was 0.2%. Both features are quite important in improving the photocatalytic properties of TiO₂.

Introduction

The modification of crystal structures of solids is becoming increasingly popular in many scientific and industrial applications. The incorporation of foreign atoms into the crystal structure of semiconductors is more attractive. In particular, the crystal structure of TiO₂ has been modified with the incorporation of altrivalent cations, which is of interest in applications such as pigments, paints, ceramics, solar energy and heterogeneous catalysis. The conversion of solar energy into chemical energy has attracted considerable research effort in recent years. The most widely investigated route is that of photochemical water cleavage in photoinduced systems. TiO₂ has been shown to be one of the most suitable materials to investigate as potential photocatalysts, because of its relatively favourable bandgap energy and high stability towards photocorrosion.

Photocatalytic performance of TiO₂ has been improved (Augustynski *et al.* 1977, Ghosh and Maruska 1977, Maruska and Ghosh 1979, Stadler and Augustynski 1979, Matsumoto *et al.* 1980, Borgarello *et al.* 1982, Kiwi and Grätzel 1986) by the incorporation of foreign atoms of higher valence, into the crystal structure. Furthermore, the light absorption and conversion capacity of TiO₂ has been extended from UV region to the visible portion of the solar spectrum due to the incorporation of foreign species. The increase of Fermi energy level of doped TiO₂, which alters the electronic interactions at the metal-semiconductor interface, believes to be the reason for these features. The increase of Fermi energy of the semiconductor implies higher electric field at the space charge region of the junction that favours the separation of the photo-produced electron-hole pairs and hence larger light conversion efficiency.

Alteration of Fermi energy level can be estimated by measuring the electrical conductivity of doped and undoped samples. It has been established (Akuburo and Verykios 1989) that the specific electrical conductivity of TiO₂ doped with cations of higher valence is significantly higher than that of undoped TiO₂. The activation energy of

electron conduction is lower when doped with higher valence cations. Similarly, it has been shown (Karakitsou and Verykios 1993) that the performance of TiO₂ as a photocatalyst in water cleavage increases, namely, the rate of hydrogen production increases, when higher valence cations (Nb⁵⁺, Ta⁵⁺, W⁶⁺) were incorporated into the crystal matrix of TiO₂. The enhancement of photocatalytic activity was found to be dependent on the concentration of the doping cation. The results were explained in terms of alteration of the bulk electronic structure of the semiconductor. The light absorption capacity, which is an important parameter that can influence the efficiency for photocatalytic water cleavage, of doped and undoped TiO₂ samples, also, has been compared (Karakitsou and Verykios 1993) using diffuse reflectance spectra. No direct correlation was observed between light absorption capacity of the semiconducting catalysts and rate of hydrogen production under photocatalytic water cleavage.

The variation of electrical conductivity of W⁶⁺ incorporated TiO₂ has been studied previously (Dharmaratna and Roshan 2002). The electrical conductivity increases significantly (by 6 orders) and the activation energy decreases by 30% as a result of doping. The light absorption capacity is studied here and we report a correlation between the activation energy and light absorption capacity of tungsten (W⁶⁺) incorporated TiO₂.

Materials and methods

Commercially available (Aldrich Chemical Company) predominantly rutile TiO₂ and WO₃ in powder form was used in the preparation of samples. TiO₂ powder, preheated at 900 °C for 5 hours to convert into 100% rutile form, was used as the parent material. Doped TiO₂ was prepared by the method of high temperature diffusion as described below. WO₃ was used as the dopant precursor. Weighted amounts of highly dispersed TiO₂ were mixed with a suspension of the dopant in distilled, deionized water. The mixture was heated gently to evaporate the water while it was stirred continuously to provide uniform mixing. The solid was grounded and heated in air at 1100 °C for 5 hours. The heating procedure involves increasing temperature at a rate of about 12 °C min⁻¹ up to 1100 °C, maintaining at this temperature for 5 hours, and slowly cooling down to room temperature overnight. This procedure was repeated for all samples with varying dopant concentration. Different samples with dopant concentration at 0.1%, 0.2%, 2% and 10% (by weight) were prepared.

Pellets (diameter ~3.0-4.0mm and length ~0.5-3.0 mm) prepared by compressing the doped powder at a pressure of about 400 atm were used for conductivity measurements. The pellets were compressed in a glass tube with spring loaded carbon electrodes. The sample was sintered overnight at 130 °C in a vacuum (1x10⁻³ m bar) in prior to the measurements of electrical conductivity. Conventional two-probe AC (1kHz and 120Hz) resistance measurements were performed at different temperatures. DC resistance was checked for a few cases and the results were same as AC measurements. The temperature range from 130 °C to 210 °C was studied. All resistance measurements were made while keeping the sample in the vacuum and when the temperature was stable and when the conductivity did not change with time. The measurements were repeated for samples doped at different concentrations.

Same samples, doped at 1100 °C, in powder form were used for the diffuse reflectance studies. A phase sensitive detection method was employed to detect the reflectance

spectra. Experimental set up consisted of a monochromator (Sciencetech, Model 9010, 200-1200 nm), a lock-in amplifier (Stanford, SR 830 DSP), a chopper (Sciencetech, C130) and an UV enhanced Si detector (Sciencetech, Si-UV-PA). Samples were placed at an angle $\sim 45^\circ$ to the chopped (53 Hz) monochromatic light beam obtained from a 100 W Q Γ lamp and the grating monochromator. Intensity of the reflected beam was measured with the detector. Reflectance spectrum was measured at a scanning speed of 4 nm/s using the fully automated system.

Results

The conductivity of pure and doped TiO₂ is purely electronic and no ionic conductivity is observed. Both AC 120Hz and 1kHz measurements gave the same result within the experimental errors and are in agreement with DC measurements. V-I characteristic curves are linear and independent of polarity. The specific conductivity (σ) of TiO₂ and doped TiO₂ vary with temperature according to the well known Arrhenius-type relationship (Equation 1) in the temperature range (130 °C – 220 °C) studied,

$$\sigma = \sigma_0 e^{-(E/kT)} \quad (1)$$

where, σ_0 is a constant, E is the activation energy of electron conduction, k is Boltzmann’s constant, and T is the absolute temperature in Kelvin.

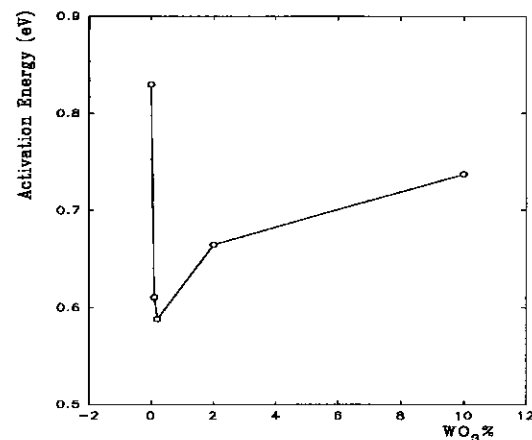


Figure 1. Variation of the activation energy with WO₃ concentration. The solid line is drawn to guide the eye.

The conductivity increased by six orders of magnitude (from 1.3×10^{-10} to $8.3 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ at 210 °C). The highest conductivity is measured when the dopant concentration is about 2%.

Activation energies of the samples, calculated from the slopes of the straight-line fits to $\ln \sigma$ verses $1/T$ plots, are shown as a function of dopant concentration in Figure 1. The activation energy depends on the dopant concentration. E decreases rapidly at lower concentrations and then increases slowly at higher dopant concentrations. The lowest activation energy, 0.67 eV, was measured when the dopant concentration was 0.2%, which is about 30% lower than that of undoped sample. It should be pointed out that the enhancement of electrical conductivity was observed only after the mixed sample was

sintered at 1100 °C for high temperature doping. See reference Dharmaratna and Roshan (2002) for more details on electrical conductivity properties

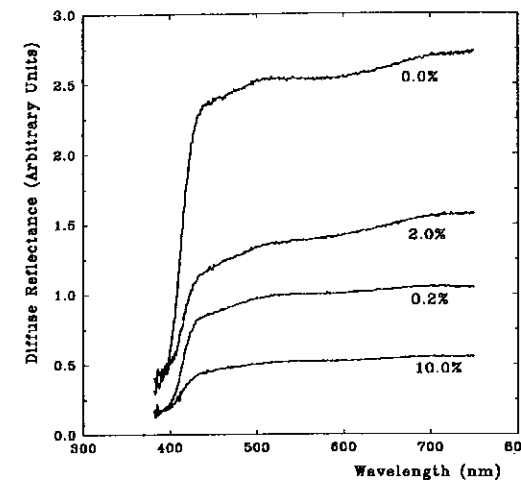


Figure 2. Diffuse reflectance spectra of doped samples at different dopant concentration.

Diffuse reflectance spectra of undoped sample and three doped samples at different dopant concentrations (0.2%, 2.0% and 10%) are compared in Figure 2. The vertical axis is in arbitrary units. It is apparent that light absorption capacity increases with the incorporation of W⁶⁺ ions into TiO₂. For TiO₂ in which the band gap energy is approximately 3.0 eV the light absorption is expected to initiate around wavelength 410 nm. Even though, our data is not sensitive enough to clearly see the onset of light absorption the result is in agreement, qualitatively.

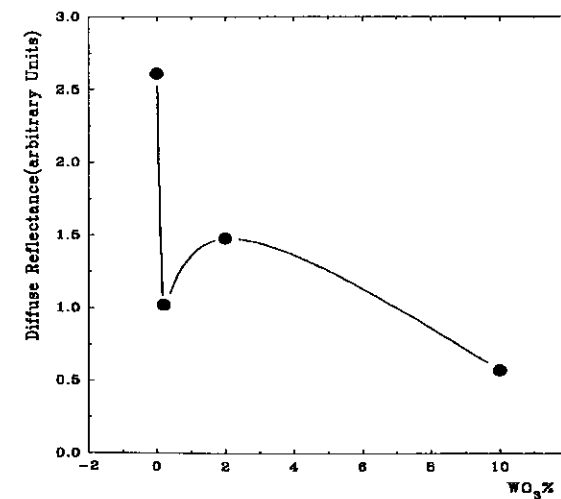


Figure 3. Variation of diffuse reflectance at wavelength 650 nm with the WO₃ concentration. The solid line is drawn to guide the eye.

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The reflectance decreases, or absorption increases, with the increase of dopant concentration. However, the light absorption capacity is not a monotonically increasing function of dopant concentration. The reflectance at 0.2%-doped sample is lower than that of at 2%-doped samples. The comparison of the diffuse reflectance at a given wavelength, 650 nm, clearly indicates that the light absorption capacity is not a monotonically increasing function of dopant concentration as shown in figure 3. A significant enhancement of light absorption is observed when the dopant concentration is 0.2%. It is very interesting to note that the activation energy was lowest at the same dopant concentration.

Conclusion and discussion

It can be concluded that the incorporation of WO₃ in to TiO₂ at high temperatures alters its electronic structure significantly. Both the electrical conductivity and light absorption capacity depend on the dopant concentration. The conductivity increased by 6 orders of magnitude and the highest conductivity was measured in the sample with 2% of WO₃. Activation energy of the sample decreased by a maximum of ~30% as a result of incorporation of WO₃ and its minimum value, 0.67eV, was measured when the dopant concentration was 0.2%.

Defuse reflectance decreases with the increase of WO₃ percentage but not in a monotonically decreasing passion. Somewhat lower reflectance was measured when the dopant concentration was 0.2% at which the activation energy was the lowest. Therefore, we claim that there is a possibility to enhance the light absorption properties while enhancing the electrical conduction properties by incorporation of proper amount of WO₃ into TiO₂. Both these features are very important in improving the photocatalytic properties of TiO₂. Further investigations are in progress to study the absorption properties of the material, because, the surface effects have to be studied in detail before making a conclusion.

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