

Effects of Ni doping on photocatalytic activity of TiO₂ thin films prepared by liquid phase deposition technique

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Abstract. The TiO₂ thin films doped by Ni uniformly and non-uniformly were prepared on glass substrate from an aqueous solution of ammonium hexa-fluoro titanate and NiF₂ by liquid phase deposition technique. The addition of boric acid as an F⁻ scavenger will shift the equilibrium to one side and thereby deposition of the film is progressed. The rate of the reaction and the nature of deposition depend on growing time and temperature. The resultant films were characterized by XRD, EDAX, UV and SEM. The result shows that the deposited films have amorphous background, which becomes crystalline at 500°C. The EDAX data confirms the existence of Ni atoms in TiO₂ matrix. XRD analysis reveals the peaks corresponding to Ni but no peak of crystalline NiO was found. The transmittance spectra of Ni uniformly and non-uniformly doped TiO₂ thin films show 'blue shift and red shift', respectively. Ni-doped TiO₂ thin films can be used as photocatalyst for the photodegradation of methyl orange dye. It was found that, organic dye undergoes degradation efficiently in presence of non-uniformly Ni-doped TiO₂ thin films when compared to uniformly doped films and pure TiO₂ films under visible light. The photocatalytic activity increases with increase in the concentration of Ni in case of non-uniformly doped thin films but decreases with the concentration when uniformly doped thin films were used.

Keywords. Ni-TiO₂ thin film; LPD technique; photodegradation.

1. Introduction

In the field of photocatalysis, the polycrystalline system formed by transition metal-ion-doped TiO₂ has been the object of several studies (Palmisano *et al* 1988; Soria *et al* 1991; Karakitsou and Verykios 1993; Choi *et al* 1994; Litter and Navio 1994, 1996). Transition metal ion doped TiO₂ thin films have been prepared by a number of physical and chemical techniques by most of the researchers (Palmisano *et al* 1988; Choi *et al* 1994; Litter *et al* 1994; Sharma *et al* 2006), but liquid phase deposition technique has not been used yet. Using LPD technique, nano sized polycrystalline films can be prepared which is of great interest to tailor this material as efficient photocatalyst to meet the present environmental crisis.

Among the different transition metal ion dopants (Fe²⁺, Zn²⁺, Zr²⁺, Nd³⁺, Co²⁺, Ni²⁺ etc), Ni²⁺ (Wang *et al* 1999; Park *et al* 2003; Jing *et al* 2005; Liu *et al* 2006; Noor Shahina Begum and Farveez Ahmed 2008) has been found to be an efficient dopant, as it possesses large surface area, crystallinity etc. On the other hand, low valence Ni²⁺ ion dopant improves the photocatalytic activity of certain semiconductor photocatalyst (Kudo and Sekizawa

2000; Sreethawong *et al* 2005). The reason for this enhancement is still not so clear but it was explained that existence of low valence Ni²⁺ greatly suppressed recombination of electron hole pair on the surface of the catalyst (Wang 1999; Jing *et al* 2005; Yu *et al* 2006) and may also partially increase surface area of the films.

In our present study, we have successfully doped Ni²⁺ into the framework of TiO₂ thin films through a simple novel technique known as LPD. The prepared film has been characterized by taking SEM, EDAX and XRD. Optical properties of doped and undoped films were compared. The photocatalytic behaviour of Ni-doped thin films was studied by applying it to methyl orange dye (Yu *et al* 2006). It was found that Ni²⁺-doped TiO₂ thin films played an important role in degradation of methyl orange dye.

More importantly, the existence of Ni²⁺ greatly suppressed recombination of electron-hole pairs on the surface of the photocatalyst. The presence of different oxidation states of dopants and a higher degree of crystallinity seems to be beneficial for retarding charge pair recombination processes in the TiO₂ lattice, hence enhancing its activity. On the other hand, non-uniformly doped Ni-TiO₂ exhibit high rate of photocatalytic activity when compared to uniformly doped TiO₂ (Yu *et al* 2006).

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2. Experimental

2.1 Preparation of Ni-doped TiO₂ thin films

The glass substrate after degreasing and cleaning ultrasonically, was placed vertically in a precursor of freshly prepared 0.1 M ammonium titanium fluoride and 0.2 M boric acid solution. The saturated solution of nickel fluoride was then mixed with precursor of different proportions (0.2, 0.3 and 0.5 at.%). The experimental solution was kept at 30°C for about 20–40 h. They were then removed and washed with double distilled water. The resultant film was homogeneous and dopant atoms were found to be distributed uniformly in the TiO₂ matrix. The films thus obtained were annealed at different temperatures. The rate of deposition depends on temperature and concentration of the precursor solution. The thickness and quality of the film was greatly accelerated when the temperature and reaction time varied. Therefore, if the reaction was carried out at 40°C for 10 h, the Ni dopant was distributed non-uniformly which can be confirmed by scanning electron micrographs (figures 3(c)–(d)).

2.2 Photocatalytic degradation

Ni-doped TiO₂ thin film was placed in aqueous solution of methyl orange taken in glass beaker. The concentration of methyl orange was about 10 ppm. The solution was exposed to sun light at different irradiation times (10–80 min). The solution was bubbled frequently with air during irradiation. The solution was scanned by UV-Vis spectrophotometer after every 10 min at the wavelength range from 300–1000 nm to measure the absorbance.

3. Characterization of deposited films

X-ray diffraction spectra were obtained from an X-ray diffractometer (type PW 3710 based tube anode: Cu, $K\alpha_1$: 1.54056 and $K\alpha_2$: 1.54439). Optical properties were studied by using UV-Vis-NIR, scanning spectrophotometer (type, Shimadzu-2003, Japan) in the wavelength range 300–1400 nm. The structural properties and elemental analysis of coating were studied using scanning electron microscope and EDAX (type: Leica Cambridge Ltd./Leica S440i for SEM and Oxford link software for EDAX).

4. Results and discussion

4.1 EDAX analysis

The elemental analysis of Ni-doped TiO₂ thin films was analysed by using electron diffraction X-ray analysis (EDAX). Figure 1 shows the EDAX spectra of Ni-doped TiO₂ thin films deposited at 30°C and annealed at 500°C.

The EDAX data confirmed that the film annealed at 500°C are nearly stoichiometric and indicates the peaks for Ti, O₂ and Ni atoms. This investigation also gave evidence that the Ni dopant is homogeneously distributed in the matrix of TiO₂.

4.2 Structure and surface morphology

Figure 2 shows the XRD patterns for Ni-doped TiO₂ thin films at different percentages of Ni and annealed at 500°C. It can be seen that the samples show only anatase

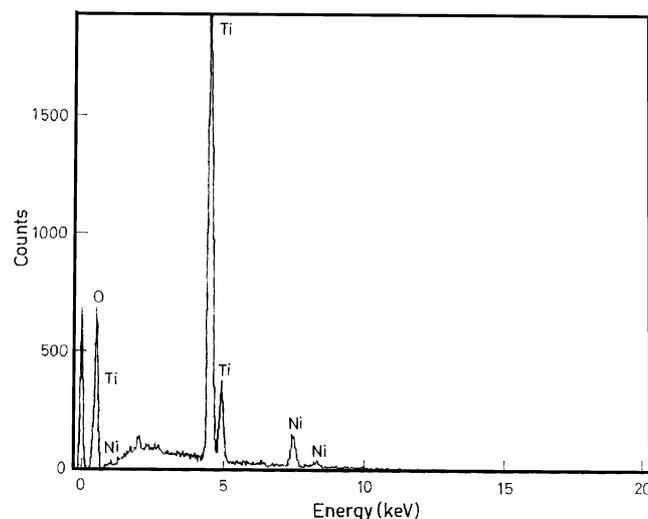


Figure 1. EDAX spectra of TiO₂ thin film doped with 0.5 at.% Ni and annealed at 500°C.

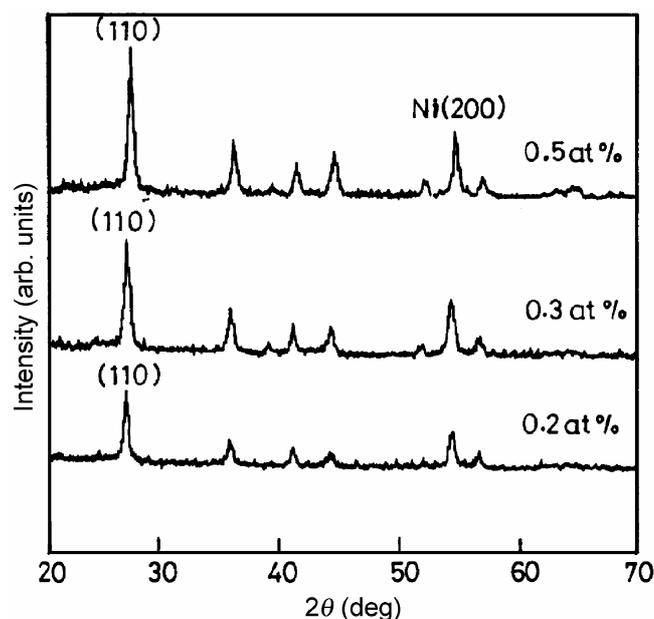


Figure 2. XRD pattern of Ni doped TiO₂ thin films at different percentage of Ni, annealed at 500°C.

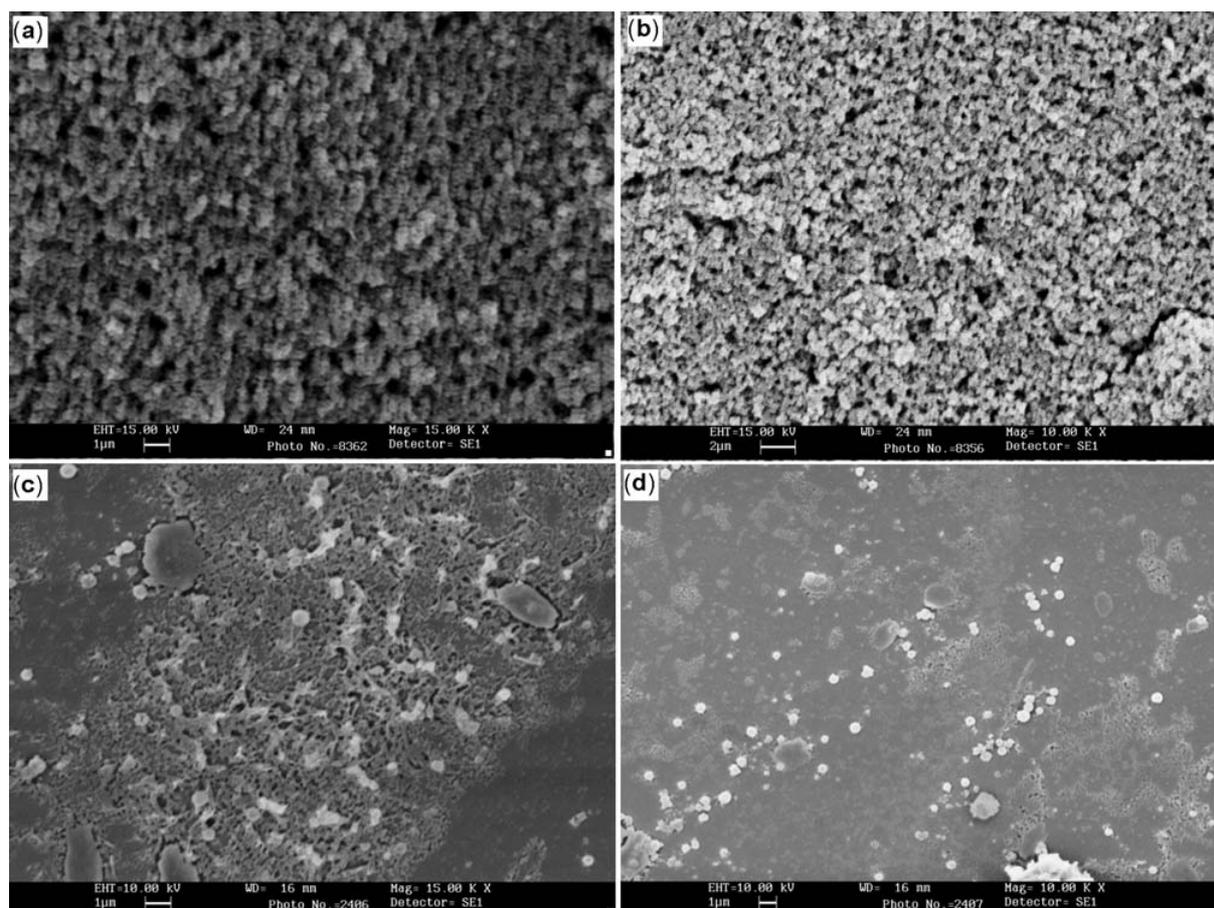


Figure 3. SEM of uniformly doped Ni–TiO₂ thin films (a) 0.3% Ni, annealed at 500°C, (b) 0.5% Ni, annealed at 500°C and SEM of non-uniformly doped Ni–TiO₂ thin films, (c) 0.3% Ni, annealed at 500°C and (d) 0.5% Ni, annealed at 500°C.

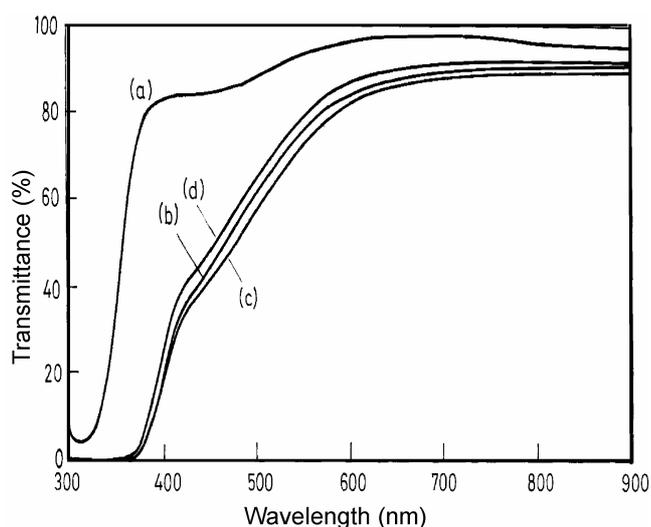


Figure 4. UV-visible transmittance spectra of Ni-doped TiO₂ thin films: (a) bare TiO₂ thin film, (b) non-uniformly doped TiO₂ thin film with 0.3 at.% Ni, (c) non-uniformly doped TiO₂ thin film with 0.5 at.% Ni and (d) uniformly doped TiO₂ thin film with 0.5 at.% Ni.

phase regardless of Ni content. The mean size of the anatase crystallites in samples can be estimated by the line broadening of the XRD peak around 25.3° using the Debye–Scherrer equation. No peaks corresponding to crystalline phase of NiO were found even at higher concentration of Ni (0.5 at.%). It was observed that Ni²⁺ has an ionic radius similar to Ti⁴⁺ and can also form octahedral coordination as Ti⁴⁺ does (Nishikawa *et al* 2001).

Surface morphology of Ni-doped TiO₂ thin films was studied by using Leica S440i scanning electron microscope with Oxford link software, used to evaluate surface topology of experimental films.

Figures 3(a)–(d) show scanning electron micrographs of uniformly and non-uniformly Ni-doped TiO₂ thin films, with different concentrations of Ni-dopant (0.3 and 0.5 at.%) and annealed at 500°C. Figures 3(a) and (b) show the compact structure with the segregation of Ni atoms uniformly in TiO₂ matrix whereas figures 3(c) and (d) show the non-uniform distribution of Ni atoms in TiO₂ framework. The average grain size is found to be 100–200 nm from scanning electron microscopic data.

4.3 Optical property

Figure 4 shows UV-Vis transmittance spectra of Ni-doped TiO₂ thin film samples of different deposition modes at 350–900 wavelength range. Red shift was observed for non-uniformly doped TiO₂ thin films at 0.5 at.% Ni concentration, whereas for uniformly doped TiO₂ thin films blue shift was viewed. It was also observed that as the concentration of dopant increases the absorption edge shifts to longer wavelength range (0.3–0.5 at.% Ni). For pure TiO₂ no such changes were observed. From the above observation, it is concluded that Ni effects the bandgap of TiO₂ (Liu *et al* 2001), but the effect varied from the doping mode. Figure 5 shows the bandgap calculation of non-uniformly doped TiO₂ thin films. From the calculation the bandgap energy of 0.5 at.% Ni-doped TiO₂ thin films is 2.9 eV against 3.2 eV of the pure TiO₂ thin films. The decrease of bandgap is the cause for red shift.

4.4 Photodegradation studies

Figure 6 shows that non-uniformly Ni-doped TiO₂ exhibits photocatalytic activity much efficiently than uniformly Ni-doped TiO₂ and pure TiO₂ thin films in the visible region. It was found that methyl orange dye undergoes decolourization effectively in presence of non-uniformly doped TiO₂ thin films with 0.5 at.% Ni dopant when compared to 0.2 and 0.3 at.% Ni dopant, whereas uniformly doped Ni-TiO₂ (figure 7) shows effective degradation with 0.3 at.% Ni when compared to pure TiO₂ thin films but the rate of degradation was very poor with 0.5 at.% Ni dopant under visible region.

The photocatalytic activity was found to be strongly influenced by the amount of Ni and the mode of deposition. Hence, the mechanism for photocatalytic activity of different samples is attributed as their charge separation efficiency; this can be explained by *p-n* junction theory (Yu *et al* 2006). The doped metallic ions may play a very important role in charge separation by capturing the electrons. In non-uniformly doped TiO₂, thin films Ni²⁺ capture the electron that left freer hole at the bottom layer. Thus, the holes concentration increases at the bottom

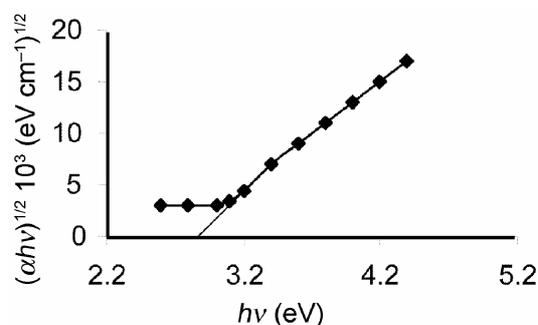


Figure 5. Bandgap energy of TiO₂, non-uniformly doped with Ni (0.5 at.%).

layer which migrates to surface layer by withdrawing the electrons from the surface. This results in the formation of inner electric field and creates *p-n* junction. Thus *p-n* junction barrier effectively (Liao *et al* 1995) prevented the recombination of electron-hole pair. It is also believed that non-uniformly doped Ni atom may partially increase the surface area of the film at an annealing temperature of 500°C. Hence photodegradation predominates.

On the other hand, in uniformly doped TiO₂ thin films, Ni²⁺ is uniformly depressed in the films. At high concentration the depressed Ni²⁺ becomes recombination centre that resists the generation of free charge carrier and hence photocatalytic activity is at its worst. But at low concentration, Ni²⁺ plays an important role in trapping the electrons and helps in charge separation, hence photocatalytic activity is comparatively good.

5. Conclusions

The thin films of Ni-doped TiO₂ were prepared by a simple novel technique known as liquid phase deposition

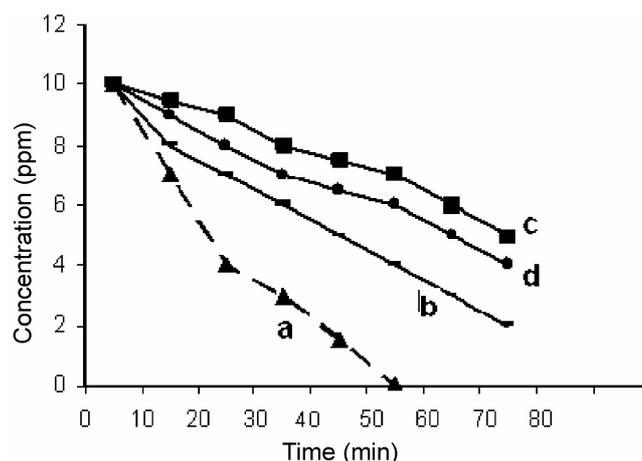


Figure 6. Photodegradation of methyl orange dye by non-uniformly doped Ni-TiO₂ films: a. with 0.5% of Ni, b. with 0.3% of Ni, c. with bare TiO₂ and d. with 0.2% Ni.

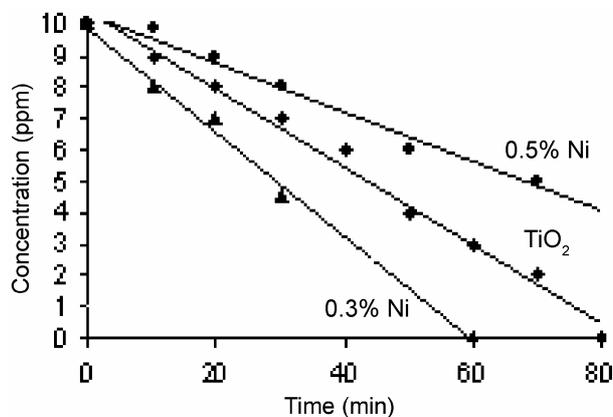


Figure 7. Photodegradation of methyl orange dye by uniformly doped Ni-TiO₂ films.

technique. The mode of deposition can be altered by varying temperature and reaction time. As a result uniformly and non-uniformly doped Ni-TiO₂ thin films were formed. The prepared films were annealed at different temperatures and characterized by taking EDAX, XRD, SEM and UV-visible spectra.

An EDAX spectrum reveals the elementary composition of films and supports the existence of Ni atoms in the TiO₂ matrix. XRD analysis shows the peak corresponding to Ni atom with the orientation [200]. Scanning electron micrographs describe the distribution of Ni atoms uniformly and non-uniformly in TiO₂ matrix at different temperatures. The non-uniformly doped Ni shows remarkable improvement in photocatalytic activity of TiO₂ thin films when compared to pure TiO₂ and uniformly doped TiO₂ thin films. The optimum concentration of non-uniformly doped TiO₂ thin films is 0.5 at. %.

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