

Comparative study of absorption band edge tailoring by cationic and anionic doping in TiO₂

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Titanium dioxide (TiO₂) is one of the most favored metal oxide semiconductors for the use as photoanode in photoelectrochemical cells (PEC) splitting the water into hydrogen and oxygen. However, the major impediment is its large bandgap that limits its utilization as photoanode. Doping has evolved as an effective strategy for tailoring optical and electronic properties of TiO₂. This paper describes the synthesis of undoped as well as iron (Fe, cationic) and nitrogen (N, anionic) doped nanocrystalline titanium dioxide by sol-gel spin coating method for solar energy absorption in the visible region. All the prepared thin films were characterized by X-ray diffraction and UV-Vis spectroscopy. Doping of both Fe and N into TiO₂ resulted in a shift of absorption band edge towards the visible region of solar spectrum.

Keywords: *nanocrystal; titanium dioxide; doping; iron; nitrogen; thin films*

1. Introduction

Titanium dioxide (TiO₂) is a transition metal oxide that occurs in three different natural forms (rutile, anatase, and brookite) as well as in five polymorphs that can be synthetically prepared [1–3]. Anatase TiO₂ has been investigated as a functional ceramics for a wide variety of applications, such as solar cells, anode materials in batteries, ceramics, photocatalysis, protective coatings, anti-reflection coatings, and optoelectronics [4–8]. It is one of the few materials that have suitable band edge positions for water splitting applications, without any need of an external bias. The conduction and valence band edges of TiO₂ match with the redox level of water. This facilitates easy transfer of charge carriers at semiconductor/electrolyte junction in PEC cell. However, photoresponse of TiO₂ is limited due to its large bandgap ~3.2 eV. This bandgap is capable of absorbing only ~4 % of incoming solar radiation [9]. Due to its large bandgap, it absorbs only the ultraviolet part of the solar spectrum.

Doping is one of the most fruitful approaches for tailoring the band gap of TiO₂ in visible regime to enhance its PEC response. Doping produces impurity states in the band gap of semiconductor to enhance visible-light absorption as well as to ensure its photoreduction activity [10]. A lot of research has been done on doping of TiO₂ with various metal ions, such as iron and copper [11–15], or non-metal species, such as silicon [16, 17], nitrogen [18, 19], phosphorus [20], carbon [21, 22], sulfur [23], boron [24], and halides [25].

Among various cationic/anionic dopants, substitution of iron (III) ions in the titania lattice is most favored [26] due to similar size of Fe³⁺ and Ti⁴⁺ ions. However, in N-doping, under optimal conditions, oxygen atoms in the TiO₂ lattice are substituted with nitrogen ions, thus, the corresponding N (2p) states are located above the valence band edge. In other words, mixing of N (2p) states with O (2p) states can take place, and the narrowing of the band gap occurs. This leads to higher photoresponse of doped TiO₂ samples under visible light irradiation.

In the present study, thin films of undoped TiO₂, Fe doped TiO₂ and N-doped TiO₂ have been

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prepared by simple, economical, sol-gel spin coating technique. The effect of doping has been studied with respect to absorption band edge.

2. Experimental

Titanium tetraisopropoxide (TTIP), ethanol, diethanolamine, iron nitrate and aqueous ammonia solution were used as received from Sigma-Aldrich, for the preparation of the sol-gel. Tin doped indium oxide (ITO) substrates were used for thin film deposition because of their electrical conductivity and optical transparency. Also, the thin films can be deposited over it easily.

A transparent gel solution of undoped/Fe doped titanium dioxide was prepared by mixing 3 mL TTIP and appropriate amount of iron nitrate (0.1 at.%, 0.2 at.%, 0.5 at.% and 1.0 at.%) in 20 mL ethanol in the presence of diethanolamine. The solution was stirred for 4 h at room temperature to enhance the reaction rate between diethanolamine and TTIP which finally converted into gel. Doping concentration was varied from 0.1 at.% to 1.0 at.% Fe.

For N-doped TiO_2 , 25 mL of aqueous ammonia solution was added slowly dropwise to 10 mL of titanium tetraisopropoxide with continuous stirring in an ice bath. Concentration of ammonia was varied from 15 % to 25 % to obtain various doping levels of nitrogen in TiO_2 . For undoped TiO_2 , the ammonia solution was replaced by double distilled water. White precipitated solution was obtained after ultrasonication and stirring for 2 h.

Few drops of prepared gel (cationic as well as anionic doping) were dropped over the substrate and the substrate was rotated at the speed of 3000 rpm for 30 s. Six such layers of films were deposited after heating each consecutive layer for about 2 min at 60 °C. The substrates were brought back to room temperature before deposition of every next layer. Final sintering was done in a microprocessor controlled electric furnace (MF-9M, Metrex Scientific Instruments (P) Ltd., New Delhi) at 500 °C for 2 h. All the prepared thin films were characterized by UV-Vis spectroscopy and X-ray diffractometry for absorption band edge determination and phase determination, respectively.

3. Results and discussion

3.1. Optical characterization

UV-Vis spectra clearly indicate red shift in absorption band edge upon introduction of Fe^{3+} ions into TiO_2 as shown in Fig. 1. Absorption band edge for undoped TiO_2 has been found to be 371 nm corresponding to band edge energy change of 3.3 eV. Introduction of Fe in TiO_2 has led to red shift in absorption band edge for all Fe doped samples as compared to undoped TiO_2 sample. The maximum shift in the band edge energy, from 371 nm to 465 nm, has been observed for 0.2 at.% Fe doped TiO_2 , corresponding to band edge energy change of 3.3 eV to 2.67 eV, respectively. The red shift in absorption band edge may be attributed to the creation of intermediate energy levels due to Fe doping as $\text{Fe}^{3+}/\text{Fe}^{2+}$ energy level lies just below the conduction band of TiO_2 and $\text{Fe}^{3+}/\text{Fe}^{4+}$ level lies just above the valence band of TiO_2 , making it a temporary trapping site for photogenerated charge carriers prolonging their recombination time, so that captured electrons or holes can be easily released from Fe^{2+} or Fe^{4+} to regenerate Fe^{3+} [27].

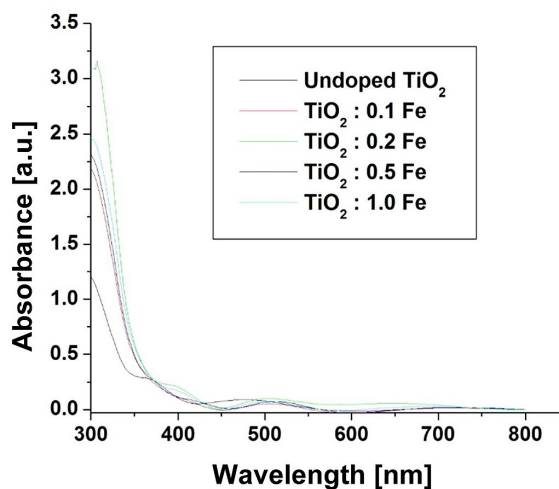


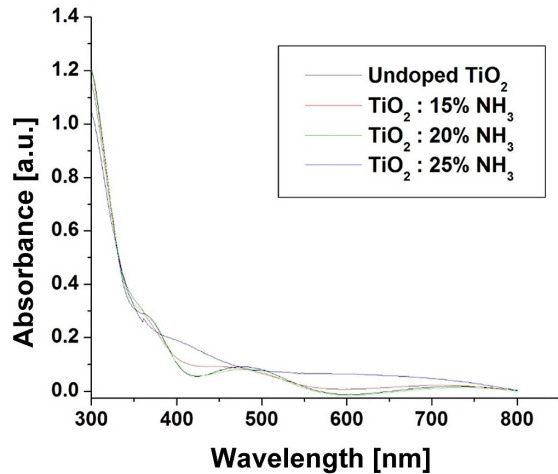
Fig. 1. Absorption spectra of undoped and Fe doped TiO_2 thin films.

Similarly, in the case of N-doped TiO_2 , all the doped samples exhibited red shift in the absorption band edge energy as compared to undoped TiO_2 sample as shown in Fig. 2. The absorption

Table 1. Optical properties of Fe and N-doped TiO₂ samples.

| Fe doped TiO ₂ sample | | | N-doped TiO ₂ sample | | |
|----------------------------------|---------------------------|-------------------------------------|--|---------------------------|-------------------------------------|
| Sample ID | Absorption band edge [nm] | Corresponding band edge energy [eV] | Sample ID | Absorption band edge [nm] | Corresponding band edge energy [eV] |
| Undoped TiO ₂ | 371 | 3.3 | Undoped TiO ₂ | 371 | 3.3 |
| TiO ₂ :0.1Fe | 423 | 2.94 | TiO ₂ :15 % NH ₃ | 443 | 2.81 |
| TiO ₂ :0.2Fe | 465 | 2.67 | TiO ₂ :20 % NH ₃ | 448 | 2.77 |
| TiO ₂ :0.5Fe | 416 | 2.98 | TiO ₂ :25 % NH ₃ | 570 | 2.18 |
| TiO ₂ :1.0Fe | 408 | 3.04 | — | — | — |

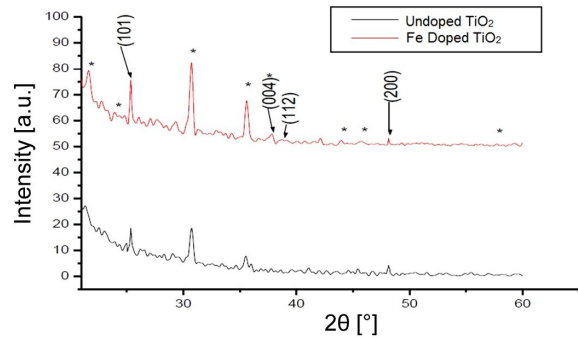
band edge shifts from 371 nm for undoped TiO₂ to 570 nm for 25 % NH₃ doped sample corresponding to band edge energy of 2.18 eV and 3.3 eV, respectively. The shift in absorption band edge energy may be due to the replacement of oxygen sites by nitrogen atoms during synthesis of TiO₂ films using NH₃ [28]. Absorption band edges and corresponding energies have been tabulated in Table 1.

Fig. 2. Absorption spectra of undoped and N-doped TiO₂.

3.2. Phase determination

All of the prepared Fe and N-doped TiO₂ samples exhibited features characteristic of an anatase TiO₂ crystallographic phase. Peaks were observed at $2\theta = 25.28^\circ$, 37.8° , 48.04° , 53.89° corresponding to (1 0 1), (0 0 4), (2 0 0) and (1 0 5) anatase

phases of TiO₂ (JCPDS Card No. 21-1272) [29] as shown in Fig. 3. The anatase phase has been retained without transformation to any other phase, even after increasing the doping concentration of iron or ammonia solution. XRD pattern shows that any other phase has not been observed. Also, no evidence of presence of iron or nitrogen was revealed which may be attributed to the presence of low amount of these elements in the TiO₂ matrix.

Fig. 3. XRD patterns for undoped and Fe doped TiO₂.

4. Conclusions

Doped TiO₂ nanostructured thin films have appeared as superior candidates for its future utilization as photoanodes in a PEC cell. Both Fe and N-doping in TiO₂ led to a reduction in the absorption band edge energy as compared to the pristine TiO₂ sample. 0.2 at.% Fe doped TiO₂ sample showed a band edge shift from 371 nm of undoped to 465 nm, corresponding to 3.3 eV to 2.67 eV, respectively. Also, 25 % NH₃ treated

TiO₂ sample exhibited an absorption band edge shift from 371 nm of undoped to 570 nm as compared to 3.3 eV and 2.18 eV, respectively. Both these doped TiO₂ samples proved to be a fruitful step in the direction of improving the suitability of TiO₂ as a promising material for solar generation of hydrogen.

The band edge shifting may be due to the additional states created in the crystal structure of TiO₂ by doping [30, 31]. N-doping causes more shift in absorption band edge towards visible region than Fe doping, which suggests that N-doping is more effective in TiO₂ for band gap narrowing as compared to Fe doping in TiO₂. Also, in case of N-doping, more shifting in the band edge may be due to the defects associated with oxygen vacancies that give rise to color centers [32].

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