AC conductivity studies of Fe doped TiO$_2$ nanotubes

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Abstract. Fe-doped TiO$_2$ nanotubes are prepared by the combination of sol-gel process with hydrothermal treatment. The morphology and crystalline structure of TiO$_2$ nanotubes are characterized by transmission electron microscopy (TEM), X-ray diffraction respectively (XRD). Fe doping induces a structural transformation from anatase to rutile. The temperature dependence of the ac electrical conductivity is investigated in the temperature range 303 - 413 K. Positive temperature coefficient of resistance is observed in the Fe doped TiO$_2$ nanotubes. PL spectrum shows the presence of oxygen vacancies and self trapped excitons in Fe doped TiO$_2$ nanotubes and undoped samples.

1. Introduction

TiO$_2$ is a wideband gap (3.22 eV) [1] n-type semiconductor with a variety of promising applications in optical and electrical devices. One dimensional nanostructure, such as nanotubes, nanowires and nanorods has attracted a great deal of attention as functional units for mediating the transport of electrons or optical excitation. Therefore, synthesizing novel one dimensional materials and probing their intrinsic properties are critical to assess their possible role in future nano device technology. In nanotubular geometries, the electronic properties of TiO$_2$ are more important, because they determine how efficiently electrons can be transferred along the one dimensional path. These features make one dimensional structures promising for applications in photo catalytic and solar energy conversion [2, 3].

Influence of various dopants (Cr, Co, Fe) on the properties of titanium dioxide has been studied by various researchers [4-6]. Bally et al reported electrical conduction in Fe doped TiO$_2$ thin films [6]. To the best of our knowledge the ac conductivity studies of Fe doped TiO$_2$ nanotubes have not been exploited yet. Electrical properties of the TiO$_2$ semiconductors are influenced by oxygen vacancies and extrinsic impurities. The main objective of the present work is to investigate the ac electrical properties of the Fe doped TiO$_2$ nanotubes for different Fe concentrations.

2. Experimental

Synthesize of Fe doped TiO$_2$ nanotubes were performed by sol gel method followed by hydrothermal method [7]. Ethanol solution of tetra butyl titanate was added drop wise to the mixture of 20 mL ethanol and 0.045 mol/L ferric nitrate. The mixture was hydrolyzed at room temperature for 2 hours under vigorous stirring, a transparent sol obtained. Gel formed after aging the sol for 12 hours at room temperature. The resulting gel was dried at 80 °C in an oven for 12 hours. After calcination of gel at 500 °C in a muffle for 3 hours Fe doped TiO$_2$ powder was obtained. Fe doped TiO$_2$ powder (1.2 g) mixed with 58 ml 10 mol/L NaOH aqueous solution in Teflon lined bottle and maintained at 150 °C for 12 hours. Obtained materials were washed with 0.1 mol/l HNO$_3$ solution and distilled water successively and dried at 80 °C, Fe doped TiO$_2$ nanotubes were obtained. Calculated Fe concentrations were 1, 7 and 16 at. % and named as Fe a, Fe b and Fe c respectively.

3. TEM analysis
The surface morphology of the TiO$_2$ nanostructures formed is shown in Fig.1, which reveals the tubular structure of synthesized Fe doped TiO$_2$ nanotubes.

![TEM images of Fe doped TiO$_2$ nanotubes](image)

**Fig.1. TEM images of Fe doped TiO$_2$ nanotubes**

4. **Structural analysis**

EDX data reveals the existence of Fe in the Fe doped TiO$_2$ nanotubes. The calculated weight percentage of Fe in the Fe doped TiO$_2$ samples are 1at.% (Fe a), 7 at.%(Fe b) and 16 at.% (Fe c).

![EDX spectrum of 16 at. % Fe doped TiO$_2$ nanotubes](image)

**Fig.2. EDX spectrum of 16 at. % Fe doped TiO$_2$ nanotubes**

5. **X-ray Diffraction Analysis**

The XRD patterns of the undoped and the Fe doped TiO$_2$ nanotubes are as shown in Fig.3. The undoped TiO$_2$ samples show only an amorphous structure. Crystallization can be seen for the Fe doped samples. 1at.% Fe doped samples have the peaks of anatase TiO$_2$. But as the Fe concentration increases the rutile peaks can be seen. From the XRD pattern it is clear that Fe doping induces anatase to rutile transformation. As the concentration of Fe increases from 1at.% to 16 at.% a slight shift of the XRD peaks towards smaller diffraction angles can be observed. The radii of the Fe$^{2+}$ and Fe$^{3+}$ are 0.75 Å and 0.64 Å respectively. The possibility for the increase in the d spacing is the presence of Fe$^{2+}$ formed by the reduction of Fe$^{3+}$ [8]. The mean crystallite size is calculated using Scherrer’s formula to be 39-63 nm.
Fig.3. XRD patterns of as synthesized TiO$_2$ nanotubes & TiO$_2$ nanotubes doped with different concentration of Fe

6. Photoluminescence Spectrum
The PL spectrum gives information on the properties of the energy levels lying within the band gap. The room temperature PL spectra of the as prepared Fe doped TiO$_2$ nanotubes under excitation with the 300 nm are displayed in Fig.4.

Fig.4. PL spectra of as synthesized TiO$_2$ nanotubes and Fe doped TiO$_2$ nanotubes with different Fe concentrations

The spectrum mainly consists of four emission bands at 388, 420, 440-460 and 486 nm. The peak at 388nm corresponds to the direct allowed transition X$_2$-X$_1$ [9]. The peaks at 420, 445, 486 and 528 nm in the Co doped TiO$_2$ nanotubes represent the defect level emissions. Peaks at 420 and 440-470 nm corresponds the emission due to the recombination of self trapped excitons [10]. Broad blue emission
ranging from 440-470 nm is due to the self trapped excitons localized on TiO$_6$ octahedra. The emission peak due to self trapped excitons for the samples Fe b and Fe c are very weak possibly resulting from the formation of rutile for the high iron concentration. The blue green emission at 486nm is be assigned to oxygen vacancies [10]. The more the oxygen vacancies the stronger the blue green emission intensity is. The sample of 16 at.% Fe concentration have low intensity peak for oxygen vacancies. Fewer oxygen vacancies in rutile than in the anatase structure were reported [6]. 1at.% Fe doped samples have higher oxygen vacancies while those of 16 at.% Fe doped samples have lower oxygen vacancies due to the formation of rutile at higher Fe concentration.

7. AC conductivity studies

To study the effect of iron doping on the ac conductivity studies of TiO$_2$ nanotube log $\sigma_{ac}$ with inverse temperature are plotted for as synthesized TiO$_2$ nanotubes and for Fe doped samples at 100Hz. We have reported the variation of ac conductivity of TiO$_2$ nanotubes with temperature and a negative temperature coefficient of resistance were observed [12]. The ac conductivity of the 7 and 16 at.% Fe doped samples are low as compared to as synthesized undoped TiO$_2$ nanotubes. In Fe doped samples the ac conductivity increases up to a particular temperature. A decrease in ac conductivity is observed for a further rise in temperature (positive temperature coefficient of resistance) in all compositions of Fe doped TiO$_2$ nanotubes. The range of temperature for transition to the positive temperature coefficient of resistance is different for different Fe concentrations. For the highest Fe concentration transition is observed at 323K and it extends up to 363K. For the undoped TiO$_2$ nanotubes this type of conductivity is not observed. So the decrease in ac conductivity with temperature can be related to the Fe concentration and the concentration of oxygen vacancies.

![Fig 7 Temperature dependence of ac conductivity of TiO$_2$ nanotubes and Fe doped samples at 100Hz](image)

In TiO$_2$, oxygen vacancies are known to be the most common defects. The positive temperature coefficient of resistance observed in Fe doped TiO$_2$ nanotube can be attributed to the formation of oxygen vacancies and the effect of Fe doping. 1 at.% Fe doped titania nanotube (Fe a) has more oxygen vacancy than the undoped samples as is confirmed by the PL. Each oxygen vacancy gives two electrons in the titania conduction band, leading to an improvement in the ac electrical conductivity.
[12]. But in Fe doped TiO$_2$ nanotubes Fe impurities act as acceptors, which decreases the electron concentration produced by oxygen vacancies [6]. For samples having higher iron concentration (Fe b& Fe c) the rutile formation lowers the oxygen vacancies, which increases the concentration of holes. The increase in concentration of holes leads to the decrease in ac conductivity after a particular temperature in Fe doped TiO$_2$ nanotubes.

Conclusions

Fe doped TiO$_2$ nanotubes with different Fe concentrations are synthesized by a sol gel method followed by a hydrothermal method. An ac conductivity data analysis is carried out in the temperature range 303-423K for the TiO$_2$ nanotubes and Fe doped TiO$_2$ nanotubes. Positive temperature coefficient of resistance is observed for Fe doped TiO$_2$ nanotubes. The range of temperature for transition to the positive temperature coefficient of resistance varies with Fe concentrations.

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References

[1] H Tang, F Levy and H Berger 1995 Urbach tail of anatase TiO$_2$ Phys. Rev. B 52 7771
[2] Y Yu and D Xu Single –crystalline TiO$_2$ nanorods: 2007 Highly active and easily recycled photocatalysts. Applied catalysis B: Environmental 73 166
[3] D Kuang, J Brillet, P Chen, M Takata, S Uchida, H Miura, K Sumioka, S M Zakeeruddin and M Gratzel 2008 Application of highly ordered TiO$_2$ nanotube arrays in flexible dye-sensitized solar cells ACS Nano 2 1113
[4] R.C dasilva, E Alves and M M Cruz 2002 Conductivity behaviour of Cr implanted TiO$_2$ Nucl.Instrum.Methods.Phys.Res.b 191 158
[5] Y Matsumoto, M Murukami, T Shono, T Hasegawa, T Fukumara, M Kawasaki, P Ahmet, T Chikyov, S Koshihara and H.Koinuma 2001 Room temperature ferromagnetism in transparent transition metal doped TiO$_2$ Science 291 854
[6] A R Bally, E N Korobeinikova, P E Schimid, F Levy and J Bussy 1998 Structural and electrical properties of Fe doped TiO$_2$ thin films J.Phys.D 31 1149
[7] L Deng, S Wang, D Liu, B Zhu, W Huang, S Wu and S Zhang 2009 Synthesis, characterization of Fe doped TiO$_2$ nanotubes with high photocatalytic activity Catal.Lett 129 513
[8] J Arana, O Gonzalez Diaz, J M Dona Rodriguez, J A Herrera Melian, C I Garriga Cabo, J Perez Pena, M Carmen Hidalgo and Jose A Navio-Santos 2003 Role of Fe$^{3+}$/Fe$^{2+}$ as TiO$_2$ dopant ions in photocatalytic degradation of carboxylic acids Journal of Molecular Catalysis A: Chemical 197 157
[9] N Daude, C Gout and C Jouannin 1977 Electronic band structure of titanium dioxide Physical Review B 15 3229
[10] Y Lei and L D Zhang 2001 Fabrication and characterization of highly ordered TiO$_2$ nanowire array J. Mater. Res 16 1138
[11] W Siripala and M Tomkiewicz 1982 Interactions between photoinduced and dark charge transfer across n-TiO$_2$-aqueous electrolyte interface J. Electrochem.Soc 129 1240
[12] P P Vijayan, M Thomas and K C George 2012 Effect of calcinations on ac conductivity studies of TiO$_2$ nanotubes J.Appl.Phys 112 104308