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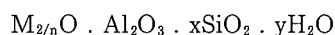
Abstract:

Thin films of TiO₂ incorporated zeolite (LZM-5) were deposited on SnO₂ coated glass and Si(100) substrates by spin-coating method using the sol consisting of TiO₂ and zeolite mixture. The thin films were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and optical UV-VIS-IR spectroscopy techniques. The spectroscopic techniques have indicated that very small nanocrystalline TiO₂ particles are able to snake through the channels of LZM-5 zeolite belonging to the Mordenite class. The TiO₂ - zeolite thin films were subjected to dye sensitization using the Ruthenium 535 bis (TBA), *cis*- bis(isothiocyano) bis(2,2'-bipyridil-4,4'-dicarboxylato) - ruthenium(II) bis-tetrabutylammonium dye to fabricate the dye-sensitized solar cells. The solar cell parameters thus obtained at AM 1.5 and 1 sun conditions are discussed.

1. Introduction:

Recently zeolites have shown a vast applications in the field of technological needs and the most prominent among them are the catalysis and detoxication of water. Zeolites have a well defined matrix type structure with uniform cavities and channels. There are more than 100 classes of zeolites. Zeolites have one more application, and that application is the incorporation of semiconducting molecules/particles in their cavities. Certain wide band gap semiconductors like TiO₂ in nano particle form exhibit excellent physical properties when incorporated in zeolite matrices. Since TiO₂ particles/molecules can be grown in extremely small size (nanometer size) by sol-gel techniques, so it is possible to study the properties of semiconducting TiO₂ molecules in zeolite matrix and the photochemical reactions resulting due to TiO₂ incorporation.

Zeolites are basically molecular sieves with selective adsorption properties capable of separating components of a mixture on the basis of a difference in molecular size and shape. The term was coined by McBain in 1932¹⁾. Molecular sieves include clays, porous glasses, microporous charcoals, active carbons, etc. Zeolites are crystalline aluminosilicates with fully cross-linked open framework structures made up of corner-sharing SiO₄ and AlO₄ tetrahedra. The first zeolite, stilbite, was discovered by Cronstedt in 1756²⁾ who found that the mineral loses water rapidly on heating and thus seems to boil. The name "zeolite" comes from the Greek words *zeo* (to boil) and *lithos* (stone). A representative empirical formula of a typical zeolite is:



where M represents the exchangeable cation of valence *n*. M is generally a group I or II ion, although other metal, non-metal and organic cations may also balance the negative charge created by the presence of Al in the structure. The framework may contain cages and channels of discrete size, which are normally occupied by water³⁾.

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In addition to Si^{4+} and Al^{3+} , other elements can also be present in the zeolitic framework. They need not be isoelectronic with Si^{4+} or Al^{3+} , but must be able to occupy framework sites. Aluminosilicate zeolites display a net negative framework charge, but other molecular sieve frameworks may be electrically neutral.

Molecular sieves have found widespread industrial applications as highly selective adsorbents, ion exchangers and, most importantly, catalysts of exceptionally high activity and selectivity in a wide range of reactions³⁾. These applications include the drying of refrigerants, removal of atmospheric pollutants such as sulphur dioxide, cryo pumping, separation of air components, separation and recovery of normal paraffin hydrocarbons, recovering radioactive ions from waste solutions, catalysis of hydrocarbon reactions and the curing of plastics and rubber. Molecular sieves exhibit appreciable Brønsted acidity with shape-selective features not available in amorphous catalysts of similar composition.

Molecular sieves are selective, high-capacity adsorbents because of their high intracrystalline surface area and strong interactions with adsorbates. Molecules of different size generally have different diffusion properties in the same molecular sieve. Molecules are separated on the basis of size and structure relative to the size and geometry of the apertures of the sieve. Molecular sieves adsorb molecules, in particular those with a permanent dipole moments, and exhibit other interactions not found in other sorbents. Different polar molecules have a different interaction with the molecular sieve framework, and may thus be separated by a particular molecular sieve. This is one of the major uses of zeolites. An example is the separation of N_2 and O_2 in the air on zeolite A, by exploiting different polarities of the two molecules³⁾.

The ring sizes of molecular sieve may be determined by sorption of molecules of different size³⁾. Water and nitrogen are two of the smallest molecules which can easily penetrate almost the entire structures. These two molecules are normally used to determine the crystallinity of molecular sieves by comparing the adsorption volume with that of a standard sample.

Zeolites with low Si/Al ratios have strongly polar

anionic frameworks. The exchangeable cations create strong local electrostatic fields and interact with highly polar molecules such as water. The cation-exchange behaviour of zeolites depends on (1) the nature of the cation species, the cation size (both anhydrous and hydrated) and cation charge, (2) the temperature, (3) the concentration of the cationic species in the solution, (4) the anion associated with the cation in solution, (5) the solvent (most exchange has been carried out in aqueous solutions, although some work has been done in organics), and (6) the structural characteristics of the particular zeolite.

Cation exchange in a zeolite is accompanied by an alteration of stability, adsorption behaviour and selectivity, catalytic activity and other properties. In some cases, the introduction of a larger or smaller cation will decrease or enlarge the pore opening. The location of that cation within the crystal will also contribute to the size of pore opening. For example, the Na^+ form of zeolite A has a smaller effective pore dimension than would be expected for its 8-membered ring framework opening. This is due to sodium ion occupancy of sites where it will partially block the 8-membered ring window. When the Na^+ ion is exchanged for the larger K^+ ion, the pore diameter is reduced so that only the very small polar molecules will be adsorbed. If the divalent Ca^{2+} cation is used to balance the framework charge, the effective pore opening widens, as only half the number of cations are needed. These ions occupy sites within the voids of the zeolite and do not reduce the effective pore diameter of the 8-membered ring. Highly and purely siliceous molecular sieves have virtually neutral frameworks, exhibit a high degree of hydrophobicity and no ion-exchange capacity.

The most important application of molecular sieves is as catalysts. Zeolites combine high acidity with shape selectivity, high surface area and high thermal stability and have been used to catalyse a variety of hydrocarbon reactions, such as cracking, hydrocracking, alkylation and isomerisation. The reactivity and selectivity of zeolites as catalysts are determined by the active sites brought about by a charge imbalance between the silicon and aluminium atoms in the framework. Each framework aluminium atom induces a potential active acid site. In addition, purely siliceous and AlPO_4 molecular sieves have Brønsted

acid sites whose weak acidity seems to be caused by the presence of terminal -OH bonds on the external surface of the crystal.

Shape selectivity, including reactant shape selectivity, product shape selectivity or transition-state shape selectivity, plays a very important role in molecular sieve catalysis. The channels and cages in a molecular sieve are similar in size to medium-sized molecules. Different sizes of channels and cages may therefore promote the diffusion of different reactants, products or transition-state species. High crystallinity and the regular channel structure are the principal features of molecular sieve catalysts. Reactant shape selectivity results from the limited diffusivity of some of the reactants, which cannot effectively enter and diffuse inside the crystal. Product shape selectivity occurs when slowly diffusing product molecules cannot rapidly escape from the crystal, and undergo secondary reactions. Restricted transition-state shape selectivity is a kinetic effect arising from the local environment around the active site: the rate constant for a certain reaction mechanism is reduced if the necessary transition state is too bulky to form readily.

Many workers^(6,7,8,9) have studied growth of TiO₂ molecules and other semiconductors in zeolite matrices but there are no reports on dye sensitized TiO₂ - zeolite thin film solar cells although there are many reports on dye sensitized nano-crystalline TiO₂ solar cells^(11,12,13,14,15).

In this paper, we present our preliminary results on the characterization of TiO₂ incorporation in zeolite such as LZM-5. A combination of Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and UV-VIS spectroscopy have been employed for the characterization of TiO₂ - Zeolite samples. The results of dye sensitized solar cells using the TiO₂ - zeolite are also discussed.

2. Experimental Section:

a) Preparation of Semiconductor-Loaded Zeolites:

The following procedure was used to prepare the TiO₂ incorporated zeolite, LZM-5. Using the molecular mass of zeolite LZM-5, Na₉(SiO₂)₂₇(AlO₂)₉·21H₂O and TiO₂ molecules, the number of channels that are available in the Zeolite, LZM-5 are calculated. Taking

the unit cell dimensions of Zeolite and TiO₂, the number of TiO₂ molecules that can be incorporated in per zeolite channel available is calculated. It is found that about 10 TiO₂ molecules per channel can be incorporated. Taking 5 grams of zeolite powder a sol is prepared with 4 cc of Titanium isopropoxide, 20 cc of ethanol at 30 °C and 1 cc of water. The sol is stirred for 24 hours and then the sol is heated for 24 hours at 80 °C in a constant temperature bath. To obtain a smoothened surface thin film for better dyesensitization, prior to thin film coating by spin coating method, 349.6 milligrams of polyethylene glycol (carbowax) was added. About 4 μm thick thin films of the zeolite incorporated TiO₂ were coated by spin coating on F doped SnO₂ glass plates and Si (100) wafers at a spin rate of 1000 rpm and annealed in air at 450 °C.

b) Characterization of Zeolite Thin Films:

The thin films were subjected to XRD, FTIR and UV-VIS optical absorption measurements to study the structure of the thin film material, to ascertain the bonding of various elements like Ti-O, Si-O, Na-O and to study the band gap of TiO₂ - zeolite composite thin film. X-ray RIGAKU set up Model No. RINT 1000 with copper K_α (1.5602 Å) radiation was used for structural characterization. For optical characterization, JASCO spectrophotometer Model No. 490 was used to study the band gap of TiO₂ thin films. For FTIR measurements Perkin Elmer FTIR spectrophotometer was used. For I-V Characteristics, the nanocrystalline TiO₂ incorporated zeolite thin films electrodes were initially subjected to thermal treatment at 100 °C and immediately immersed in dye to prevent the electrodes from rehydration from the surrounding air which can degrade the cell performance. The TiO₂-zeolite thin films were subjected to dye sensitization in ruthenium 535 bis TBA), *cis*- bis (isothiocyanato)bis(2,2'-bipyridil-4,4'-dicarboxylato)-ruthenium(II)bis-tetrabutylammonium, purchased from Solaronix and was used as received. The dye was dissolved in dry ethanol at a concentration of 0.2 g/l. Nanocrystalline TiO₂ incorporated zeolite thin films electrodes were kept immersed in the dye solution for 3 hours at 60 °C. The dyesensitized solar cell was prepared by making a module where two narrow strips of about 2mm of sealing material, Amosil-4 were placed

on the two sides of the TiO_2 thin films and platinized F doped SnO_2 coated glass was placed on the top as the counter electrode. The two electrodes were clamped tightly together. The set up was left in an air tight box for 24 hours so that the system remains compact. Electrical connections were made with copper wire using silver paste contacts with TiO_2 thin film and the counter electrode.

3. Results and Discussion:

a) X-ray Diffraction:

Figure 1a shows the X-ray diffraction spectra of the as grown TiO_2 thin films, zeolite powder and zeolite incorporated TiO_2 thin films. The characteristic peak of (101) oriented TiO_2 thin film is seen confirming the anatase phase formation. Figure 1b shows the TiO_2 incorporated zeolite thin film which exhibits other peaks apart from a small intensity anatase peak revealing that there are some molecules of TiO_2 which have been incorporated into the cavities of Zeolite and some TiO_2 molecules may be there at the surface of the zeolite thin films exhibiting a reduction in the peak height which clearly infers the incorporation of TiO_2 molecules inside the zeolite cavities. Also the decrease in the crystallinity of the zeolite pattern upon TiO_2 incorporation reveals some of the alkali atoms have been replaced with positively charged Ti species of the TiO_2 molecule⁴. The preparation procedure does not involve the use of high amount of water thus assuring that the Ti species can be incorporated into almost all available Zeolite cavities. The pattern of the Zeolite LZM-5 powder spectra show various peaks which tally with the values given in the literature¹⁰.

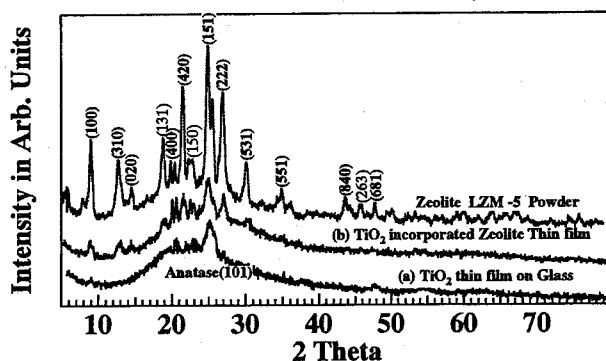


Fig.1. XRD pattern of (a) TiO_2 thin film on glass (b) TiO_2 incorporated zeolite thin film (c) zeolite LZM-5 Powder.

b) FTIR :

Figure 2 shows the FTIR spectra of TiO_2 incorporated zeolite thin films deposited on silicon. The as-grown thin films exhibit the characteristic bonding of the $\text{Ti}=\text{O}$ (450cm^{-1}), $\text{Ti}-\text{O}-\text{Ti}$ (810cm^{-1}), $\text{O}-\text{T}-\text{O}$ ($\text{T}=\text{Si}, \text{Al}$), $\text{T}-\text{O}-\text{Si}$ (1025cm^{-1}), $\text{Na}-\text{O}$ (2350cm^{-1}). According to Beattie and Faecett⁴ the monomer $\text{Ti}-\text{O}$ and $\text{Ti}=\text{O}$ stretching vibrations are 550cm^{-1} and 450cm^{-1} respectively and the $\text{Ti}-\text{O}-\text{Ti}$ linkage vibration is around 850cm^{-1} . Thus comparing these values with our data suggests that TiO^{2+} species and Titanium in the form $\text{O}-\text{T}-\text{O}$ (where $\text{T}=\text{Si}$ or Al) are incorporated into the zeolite framework. The spectrum also shows a slight shift of $\text{T}-\text{O}-\text{T}$ ($\text{T}=\text{Si}, \text{Al}$) stretching vibrations of the framework at around 1000cm^{-1} and shows the effect of Ti species on the Zeolite framework.

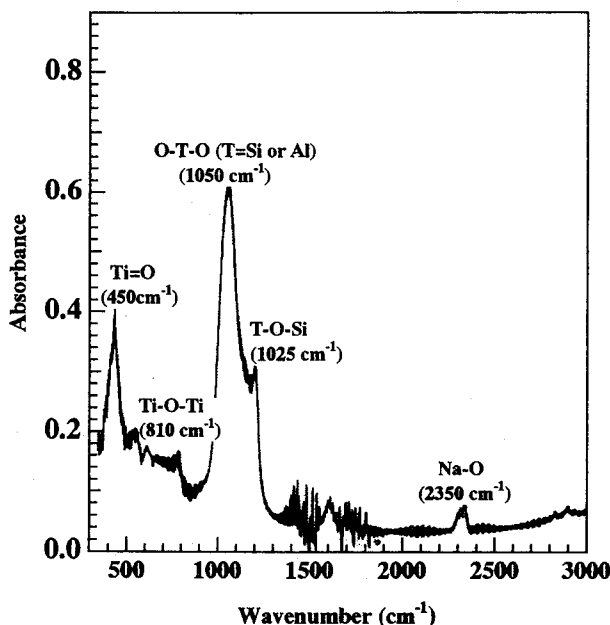


Fig.2. FTIR spectrum of TiO_2 incorporated zeolite LZM-5 thin film on Si(100) wafer.

c) Optical:

From the diffuse reflectance spectra of the TiO_2 exchanged Zeolite thin films in the range of 300 to 800 nm, assuming the transmittance of the zeolite films to be ≈ 0 the following equation was used for calculation of optical absorption coefficient, α :

$$T = (1 - R) \exp(-\alpha x) \quad (1)$$

Where T = Transmittance, R = Reflectance and " x " is the thickness of the thin film.

A plot of α vs $h\nu$ (Fig. 3) and $(\alpha h\nu)^{1/2}$ vs $h\nu$ (Fig. 4) are plotted. It is seen that from Fig. 3 the onset of

the absorption starts from 3.15 eV and from Fig. 4 the band edge gets shifted to nearly 3.35 eV. The reason for this blue shift is that on the incorporation of TiO₂ into the cavities of the LZM-5 mordenite zeolite can be explained by the quantum size effects as indicated in CdS and other semiconductor materials⁹. This quantum size effect is due to charge carrier confinement, and it leads to a change of optical properties of small particles⁹. A comparison of the above results with the XRD results suggest that the sizes of the Ti species in our TiO₂ - zeolite samples are of nanometric dimensions. Redox polyiodide electrolyte was inserted from the sides using microsyringe. All the I-V characteristics were measured under AM1.5 white light illumination.

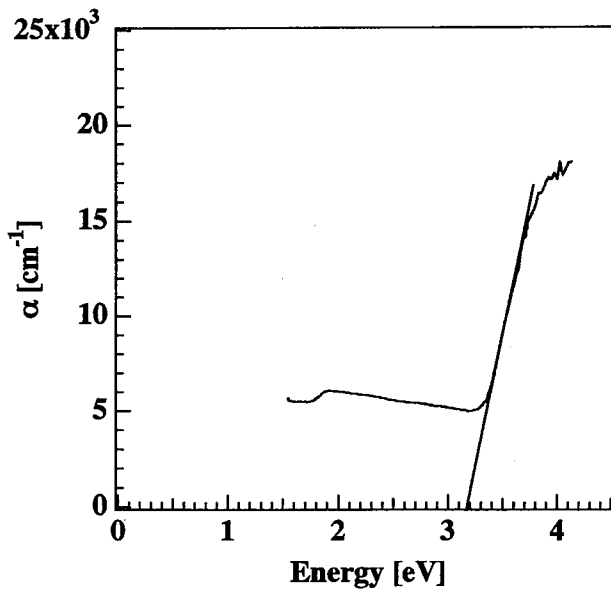


Fig.3. A plot of optical absorption coefficient, " α " vs energy for a TiO₂ incorporated zeolite LZM-5 thin film.

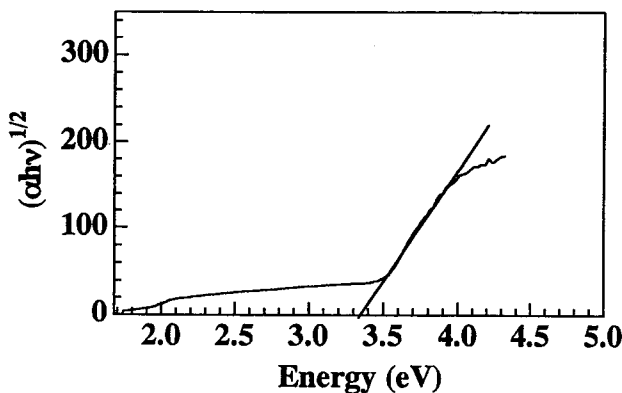


Fig.4. A plot of optical absorption coefficient, $(\alpha\nu)^{1/2}$ vs energy for a TiO₂ incorporated zeolite LZM-5 thin film.

d) I-V Characteristics:

The I-V Characteristics were performed on the dye sensitized TiO₂ - zeolite thin film solar cells both under dark and illumination. The following redox electrolyte compositions were used:

- (i) 0.3M LiI, 0.03M I₂, acetonitrile 60 wt% and NMO (3-Methyl-2-oxazolidinone) 40 wt%
- (ii) 0.3M LiI, 0.03M I₂, Acetonitrile 100 vol% and TBP (tertiary-butylpyridine) 3 vol%

It is seen from the Fig. 5 for a polyiodide electrolyte composition of (i) and solar cell area of 0.28 cm² the efficiency is 0.425%.

It is also seen from the Fig. 6 for a polyiodide electrolyte composition of (ii) the efficiency is 0.292%.

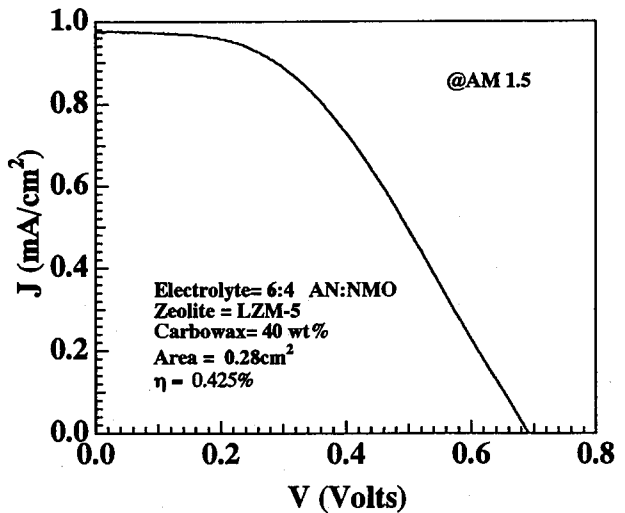


Fig.5. I-V plot of dye sensitized solar cell for polyiodide composition of 6:4 AN:NMO

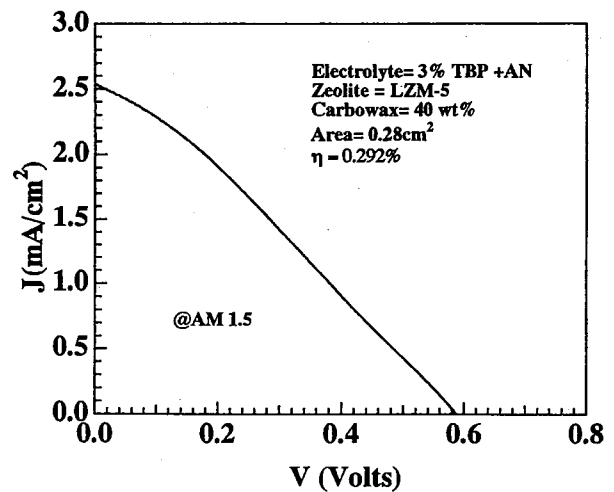


Fig.6. I-V plot of dye sensitized solar cell for polyiodide composition of 3 Vol.% TBP + AN.

From the above results we see that the solar power conversion efficiencies are very low. There are several reasons for the low values of the power conversion efficiency. Size of the TiO_2 molecules/particles introduced into the zeolite matrices have to be consistent with the columnar dimensions of the cavities thus there can be agglomeration of small cavities containing particles of TiO_2 must have occurred producing materials that can "snake" through the cavities of the zeolites thus many of the absorbed dye molecules do not have proper contact with the semiconducting TiO_2 molecules. Also the zeolite matrix being a silicate matrix, itself being an insulator acts as a barrier for the dye molecules to be in contact with each other in the lateral directional cavities. Since the cavity dimension are of a few nanometers so only small TiO_2 particles could have formed in them thus effective interaction with dye molecules is reduced for solar power conversion.

4. Conclusions:

This paper describes a viable method for the incorporation of TiO_2 in the zeolite LZM-5 matrix by synthesizing nanometer scale TiO_2 prepared by spin coating technique using the colloidal sols of TiO_2 - zeolites with proper composition. It is found from XRD, FTIR and UV-VIS optical absorption techniques, that the Zeolite matrix do contain TiO_2 molecules.

A shift of the band gap of the TiO_2 -zeolite thin film indicates that the particles incorporated into the zeolite matrix are very small and slightly change the zeolite structure. The dye sensitized nanocrystalline thin film solar cells yield low efficiencies of about 0.425%. Further work on the TiO_2 presence in zeolite matrices is in progress.

References:

1. J. W. McBain, *The Sorption of Gases and Vapors by Solids*, Rutledge, London, ch. 5, (1932).
2. A. F. Cronstedt, *Acad. Handl. Stockholm*, 17, 120 (1756).
3. D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, John Wiley, London, (1974).
4. I. R. Beattie and V. Faecett, *J. Chem. Soc. A.*, 1583(1967).
5. L. E. Brus, *J. Chem. Phys.*, 79, 5566(1983).
6. C. R. Berry, *Phys. Review.*, 161, 848(1967).
7. Marye Anne Fox and Thomas L. Pettit, *Langmuir*, 5, 1056(1989).
8. Xincheng Liu, Kai-Kong lu and J. Kerry Thomas, *J. Chem. Soc. Faraday Trans.*, 89 (11), 1861 (1983).
9. H. Chen, A. Matsumoto, N. Nishimiya, K. Tsutsumi, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 157, 295 (1999).
10. V. Gramlich, PhD dissertation, ETH, Zurich, (1971).
11. B. O Reagen and M. Gratzel, *Nature*, 353, 737 (1991).
12. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Gratzel, *J. Am. Chem. Soc.* 115, 6382 (1993).
13. M. M. Rahman, K. Murali Krishna, T. Miki, T. Soga, K. Igarashi, S. Tanemura and M. Umeno, *Solar Energy. Mater. Solar Cells*, 48, 123 (1997).
14. M. M. Rahman, G. Yu, K. Murali Krishna, T. Soga, J. Watanabe, T. Jimbo and M. Umeno, *Appl. Optics*, OT 37, 691(1998).
15. M. M. Rahman, K. Murali Krishna, T. Soga, T. Jimbo and M. Umeno, *J. Phys. Chem. Solids.*, 60, 201(1999).