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Sol-Gel Synthesis and Characterization of TiO_2 Nano Films in the Building of Dssc

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Abstract: *Dye-sensitized solar cells (DSCs) promise a short energy- payback time and offer a potential low-cost alternative to conventional photovoltaic devices based on semiconductors. This work describes the effort which has mainly been developed on DSSC solar cells with suitable dye for light harvesting and interfacial electron transfer processes with nano crystalline wide band-gap semiconductors. The photo anode preparation has been done by means of TiO_2 nano films by sol gel method using TTIP as precursor, and coated in ITO plate by doctor blading technique. The mesoporous TiO_2 thin film was characterized by XRD, SEM, and TEM. A novel unique combination of electrolyte is used (0.6 M of EMII, BMII and PMII, 0.1 M LiI, 0.05 M I2 in acetonitrile). The best performance was demonstrated by the DSSC having a 16μm-thick TiO_2 back electrode, which gave a solar energy conversion efficiency of 1.83% under the light of intensity of 100 $mWcm^{-2}$.*
Key words: *Electrolyte, Indigo Dye, Sol-gel, TiO_2, XRD,*

I. Introduction

As the most promising photo catalyst, TiO_2 materials are expected to play an important role in solving many serious environmental and pollution challenges [1]. TiO_2 also bears tremendous hope in helping ease the energy crisis through effective utilization of solar energy based photovoltaic devices. Titanium dioxide (TiO_2) has been widely investigated as a key material for applications in photovoltaic cells, batteries, chemical sensing, optical emissions, photonic crystals, catalysis, photo catalysis and environmental purification. Anatase TiO_2 electrodes are used in solar cells, lithium batteries and electro chromic devices owing to its good storage capacity, cycling-stability and safety against overcharging [2]. Non-toxicity, environmental compatibility and low price are other practical advantages of TiO_2.

In DSSC, the light absorption and the separation of the electrical charges happens in different process. The light absorption process is performed by dye molecules, and the separation of the electrical charge is done by the nanocrystal inorganic semiconductor TNP (titanium dioxide nanoparticles) that has a wide band gap [3]. This TiO_2 working electrode film is an important part of DSSC. It can be prepared by various methods such as solgel, chemical vapor deposition (CVD) and sputtering. Sol-gel process is a favorable method for preparing TiO_2 nano particles, since the composition, particle size, film thickness, and porosity of TiO_2 can be easily controlled by adjusting parameters such as sol concentration, hydrothermal growth temperature, and sintering condition. We prepared TiO_2 naoparticles by Sol-gel- process and its characterization has been studied.

Although the DSCs using noble metal complexes as dye sensitizers provided relatively high efficiency, there are many disadvantages for using noble metals in the DSCs, such as limited resource, high cost, and long-term unavailability. In nature, flowers, leaves, and fruits show various color and contain various natural dyes which can be extracted by simple procedure. Therefore, researchers pay more and more attention to natural dyes owing to their low cost, non toxicity, and full biodegradation [4-11]. In our work, we synthesized natural indigo Dye and used as sensitizer. Using this dye, the incident monochromatic photon-to-current conversion efficiency (IPCE) is impressive (IPCE) value exceeds 80% in the wavelength range between 230-284 nm.

The presence of a liquid electrolyte demands a perfect seal in order to avoid leakage and evaporation of the solvent. Nonetheless, such perfect seals are difficult to obtain, usually the use of a liquid component results in poor long-term stability. Many efforts have been investigated to overcome this drawback by replacing the liquid electrolyte by room temperature ionic liquids, organic and inorganic hole transport materials, polymer and gel electrolytes. DSSC using polymer gel electrolytes present a better performance when compared to the same device assembled with a classical polymer electrolyte. So a new combination of redox electrolyte, consisting of [0.6 M of EMII (1- Ethyl-3- methyl – imadazolium iodide), BMII(1-butyl-3-methyl–imadazoliumiodide) and PMII (1-propyl-3-methyl-imidazoliumIodide), 0.1 M LiI, 0.05 M I2 in acetonitrile was introduced into the cell through one of two small holes drilled in the counter electrode.

Counter electrode with high electrochemical activity is an important requirement of efficient DSSCs. Cobalt sulphide is used as Counter electrode.

II. Experimental

2.1. Materials

Titanium (IV) isopropoxide is used as (TTIP, 97%, Aldrich), precursors for preparing titanium dioxide by sol-gel method. The adjustment of pH was done by adding reagent grade NaOH (Aldrich). Triton X-100 (Aldrich) and Polyethylene glycol (PEG M.W=20,000, Aldrich) were used as binders, and natural dye Indigo dye was used as the sensitizer. The electrolyte 0.3 M LiI, 15 mM I2, 0.5 M PMII, BMII, PMII polymer gel electrolyte was purchased from Aldrich. Acetic acid and ethanol were purchased from Aldrich, 0.5mM Cobalt Sulphide (Aldrich). All other solvents and reagents were analytical grade quality, purchased commercially, and used without any further purification. ITO conducting glass (20~30 Ω/cm2, Aldrich, Co., LTd) was selected as the substrate for TiO_2 film.

2.2. Synthesis of nano crystalline anatase TiO_2 powder

TiO_2 mesoporous nanoparticles were prepared by titanium tetraisopoxide (TTIP) 27 ml in 100 ml of n-heptane as a solvent and stirring for 2 h. Then 7.98 ml of double distilled water was added drop wise and the molar ratio of TTIP: H_2O was maintained as 1:5, and then this sample was aged for 72 h at room temperature, and then dried at 70 °C for 12 h and calcinated at 400 °C, 600 °C and 700 °C in the ambient air [12]. The obtained TiO_2 were studied through XRD, SEM and TEM. The sample heated at 400°C was used in the preparation of photo anode because it has anatase nano crystalline structure of particle size 10 nm.

2.3 Preparation of TiO_2 Photo anode

For the preparation of mesoporous TiO_2 nanocrystalline film, first the titania slurry was prepared by the incremental addition of 2 ml aqueous Triton X solution to 0.5 g mesoporous TiO_2 powder in a mortar under vigorous grinding by the pestle and the prepared uniform slurry was coated on ITO glass by a doctor blade technique. Triton X acts as a binder to prevent cracking of film and control the porosity during preparation of film. After natural drying at room temperature, the thin film was calcined in static air at 400 °C for 30 min.

2.4 Fabrication of DSSC

The mesoporous titania electrode was immersed in the ethanolic solution of indigo dye at room temperature for 24 h in the dark. The electrode was then rinsed with ethanol. The counter electrode was prepared by spin coating 5mM solution of Cobalt sulphide in Indium Tin oxide plate and sintering for 30 min at 900°C. The resulting dye adsorbed film was clipped with the counter electrode and then redox electrolyte containing 0.3M LiI, 15mM I2, 0.5 M (PMII+EMII +BMII) and 0.2 M Poly ethylene glycol in acetonitrile, was introduced into the cell through one of two small holes drilled in the counter electrode through capillary action [13].

III. Characterization

The crystallinity and crystal phase of the titania film was evaluated by Bruker D8 Discover XRD with diffracted beam graphite monochromator at 50 kV and 40 mA (Cu K α with λ = 1.54187 Å).

The film thickness was measured by a profilometer (Veeco, dektack3). The microstructure of films was studied by transmission electron microscopy (TEM) Jeol JEM 2100 Resolution: 1.4A˚ (Lattice) to 1.9A˚ and Scanning Electron Microscope (SEM) HITACHI Model S-3000H [14]. The photo-electrochemical properties of the solar cell were studied by recording the current–voltage characteristics of the cell under an illumination of 1 Sun (100 mW/cm^2) using a 150W Xenon lamp (Polaronoix).

3.1 Results and discussion

3.1.1 XRD Analysis

The XRD patterns of the synthesized TiO_2 nano powders calcined at 400°C, 600°C and 800°C for 3 h are shown in Fig. 1, which revealed the presence of anatase and/or rutile phases of TiO_2 depending on the calcination temperatures. At 400°C and 600 °C, it is clear that a peak was recorded at 2θ value of 24.882◦, which corresponds to crystalline anatase phase of TiO_2. The crystallite size of TiO_2 was calculated from a half-value width of the XRD peak at 2θ = 25.3 using Scherrer's equation.

$$D = \frac{0.94\lambda}{\beta \cos\theta} \qquad \text{Equation (1)}$$

where K (0.94) is the shape factor, λ is the x-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle, D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size [14-16].

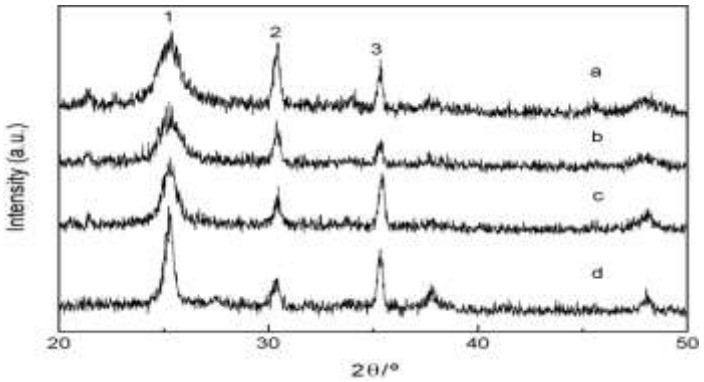

Fig.1: XRD diffraction of TiO_2 calcining at 400°C (a), 600°C (b), 800°C (c) and P25 (d)

Using the Scherrer's formula mentioned above at λ = 1.5418A°, β = 0.774˚, 2θ = 24.92˚, the crystallite size of the synthesized TiO_2 powder was found to be 10.5 nm. The anatase titania crystal with peaks at 2θ of 25.3, 38.0 and 48.3 corresponding to (101), (004) and (200) phases respectively. With the decrease of grain size, XRD peak broadens. So, the broadness of the diffraction peaks at 400°C (a) shows the decrease of crystal size, at calcinations temperature of 600°C (b), 800°C (b), and commercial P25 (d) diffractions peaks becomes narrower clearly showing the bigger size of particle due to the sintering effect which is illustrated in Table 1, however no rutile phase were observed even at higher temperature showing clear maintenance of good crystal framework of the anatase titania. In XRD patterns there were no impurities or reaction product peaks observed indicating that the obtained materials are in pure titania form.

Table 1. Variation of nano size TiO_2 with Temperature

Temperature	Crystal size (nm)
400°C	10.5nm
600ºC	55m
800ºC	100nm

3.1.2 TEM Analysis

It is clear from TEM images in fig 2, the smaller particles with pores were observed in the 400°C calcined samples, however in the case of 600°C samples and 800°C, scattered large particles of sizes 40–100 nm with tetragonal structures were observed, which clearly shows the interconnection of the mesopores were vanishing with the shrinkage in diameters of the pores at all over the surfaces. This is also consistent with the XRD patterns [17-19].

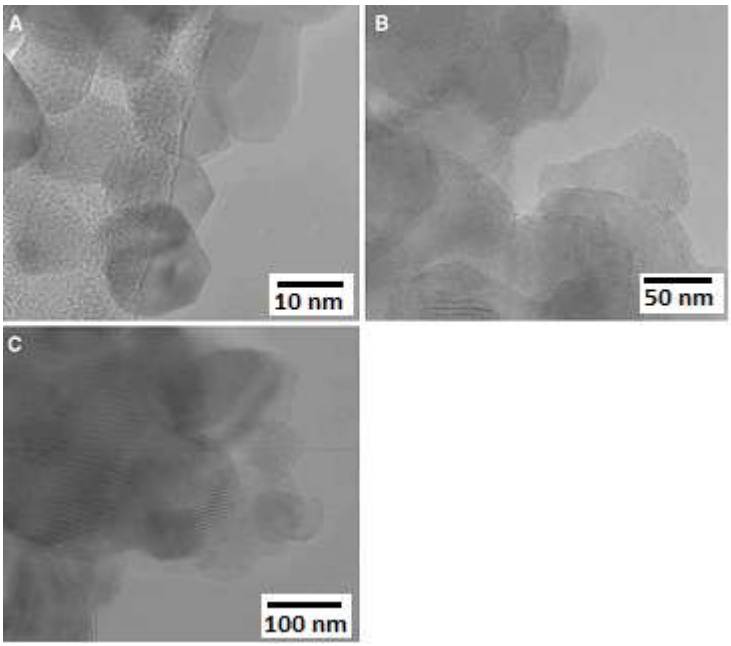

Fig.2: TEM images of TiO_2 calcined at400°C (a), 600 °C (b) and 800°C (c)

3.1.3 SEM analysis

Fig 3 shows the SEM analysis in which the particle size is around 10- 20 nm which is calcined at 400°C. Since a crystallite can be defined by studying the orientation of the lattice fringes, one can see the average grain size in the synthesized TiO_2 powder is about 10-20 nm in diameter, which is in good agreement with the calculated value from XRD analysis.

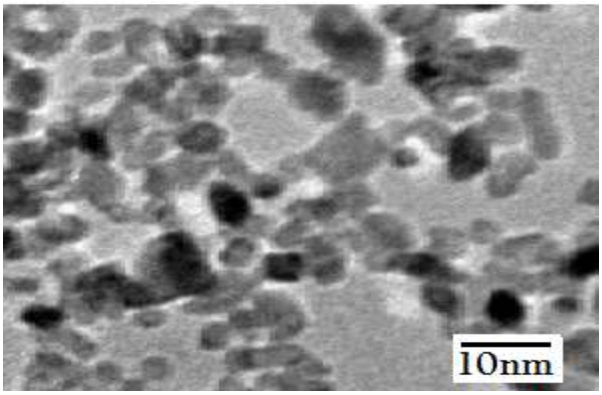

Fig.3. SEM images if TiO_2 calcined at 400 □C

3.1.4 Photo catalytic activity

These nano particles are coated in ITO plate and from this fabricated DSSC, the photocatalytic analysis is measured. Fig. 4 shows the photocurrent and photo voltage curves of the cells under the illumination (100 mW/cm2). The cell gave a high short circuit current (I_{SC}) of 4.3 mA/cm^2, an open circuit voltage 650 mV and a fill factor of 66%, yielding over all conversion efficiency of 1.83% is determined using equation (3),

$$FF = \frac{ImxVm}{IscxVoc} \qquad \text{Equation (2)}$$

Where FF is the fill factor, I_{sc} is short circuit current, V_{oc} is the open circuit voltage, I_m is the maximum current and V_m is the maximum voltage,

$$\eta = \frac{Voc \times Jsc \times FF}{Pin} \qquad \text{Equation (3)}$$

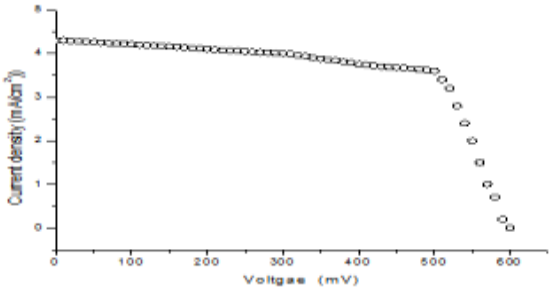

Fig. 4 Photovoltaic performance of TiO_2 nanoparticles

Table 2. Photovoltaic performance of TiO2 nanoparticles

Voc(mV)	Jsc(mA/cm^2)	FF	η%
650	4.3	0.66	1.83

IV. Conclusion

At the hydrolysis stage, the water quantity controls the generated grain sizes; with the slow addition and limited quantity of water we can control the morphologies of sol–gel derived materials. It is also well known that the high pore volume and large surface area of semiconducting materials are necessary to provide sufficient light and dye absorption, for better electrical connection with redox electrolytes, crystallinity and the photocurrent density. At the appropriate calcinations temperature, the n-heptane solvent can be removed and only mesoprous titania is observed. The calcined and optimized mesoporous substrate used in the fabrication of dye-sensitized solar cell which gave a fill factor of 66% with an energy conversion efficiency of 1.83% under 1 sun irradiation. The mesopore TiO_2 substrate provide better surface for the absorption of dye, which improves

light absorption efficiency and charge injection dye to conduction band of semiconductor leading to high efficiency anode material in dye-sensitized solar cells.

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References

[1] B.O'Regan,M.Gratzel, "A low cost high efficiency solar cell based on dye- sensitized colloidal TiO_2 films", Nature 353(1991)737–740.
[2] M.K.Nazeeruddin,A.Kay,I.Rodicio,R.Humphry-Baker,E.Muller,P.Liska,N.Vlachopoulos,M.Gratzel, "Conversion of light to electricity by cis-X_2-bis (2,20- bipyridyl-4,40-dicarboxalate) ruthenium (II) charge transfer sensitizers on nanocrystalline TiO_2 electrodes", J.Am. Chem. Soc.115 (1993) 6382–6390.
[3] B.Y. Wei, H.M. Lin, C.C. Kao, A.K. Li, "Effect of calcinations on photo catalytic activity of TiO_2 nanopowders", J. Mater. Sci. Eng. 35 (2003) 64–69.
[4] Y.Li,J.Hagen, W. Schaffrath, P. Otschik, D. Haarer, "Titanium dioxide films for sensitized photovoltaic cells derived from a sol–gel process", Sol. Energy Mater. Sol. Cells 56 (1999) 167–174.
[5] M.Gratzel, "Dye sensitized solar cell", Photoelectrochemicalcells, Nature414 (2001)338–344.
[6] E.W. McFarland, K. Tang, "A photovoltaic device structure based on internal TiO_2 solar cells by chlorophyll derivatives", J. Phys. Chem. 98 (1994).
[7] M. Sakanoue, Y. Kinoshita, Y. Otsuka, and H. Imai, "Photocatalytic activities of rutile and anatase nanoparticles selectively prepared from an aqueous solution", Journal of the Ceramic Society of Japan, vol. 115, no. 1348, pp. 821–825, 2007.
[8] M. H. Habibi, N. Talebian, and J.-H. Choi, "The effect of annealing on photocatalytic properties of nanostructured titanium dioxide thin films", Dyes and Pigments,vol. 73, no.1, pp. 103–110, 2007.
[9] H. Han, X. Zhao, J. Liu, "Enhancement in photoelectric conversion properties of the dye-sensitized nanocrystalline solar cells based on the hybrid TiO_2 electrode", Journal of The Electrochemical Society 152 (2005) A164–A166
[10] C. Grimes, G. Mor, O. Varghese, M. Paulose and K. Shankar, "A review on highly ordered, vertically oriented TiO2nanotube arrays: Fabrication, material properties, and solar energy applications", Solar Energy Materials and Solar Cells, 90, (2006) pp. 2011-2075.
[11] M. Wei, Y. Konishi, H. Zhou, H. Sugihara, H. Arakawab, "Utilization of titanate nanotubes as an electrode material in dye-sensitized solar cells", Journal of The Electrochemical Society 153 (2006) A1232–A1236.
[12] G.S. Kim, H.K. Seo, V.P. Godble, Y.S. Kim, O.B. Yang, H.S. Shin, "Electrophoretic deposition of titanate nanotubes from commercial titania nanoparticles: application to dye-sensitized solar cells", Electrochemistry Communications 8 (2006), 961–966.
[13] G.Rothenberger, P. Comte, M. Gratzel, "A Contribution to the Optical Design of Dye-Sensitized Nanocrystalline Solar Cells", Solar Energy Materials and Solar Cells58, (1999) pp. 321-336.
[14] Alam Khan M., Shaheer Akhtar, M., Bong Yang, O., 2010, "Synthesis, characterization and application of sol–gel derived mesoporous TiO_2 nanoparticles for dye-sensitized solar cells", Solar Energy, 84, pp 2195–2201.
[15] M. Adachi, Y. Murata, I. Okada, S. Yoshikawa, "Formation of Titania Nanotubes and Applications for Dye-Sensitized Solar Cells", J. Electrochem. Soc. 150 [8] (2003) G488-493.
[16] C. Longo and M. DePaoli, "Dye-Sensitized Solar Cells: A Successful Combination of Materials", J. Braz. Chem. Soc., 14 (6) (2003) pp 889-901.
[17] Martinson, Alex. B.F.;Hamann, T.W,Pellin, et al," New Architectures for Dye-SensitizedSolarCells,"Chem-Eur.J,vol.14,pp.4458-4467,2008
[18] W. Chan, "Titania nanotube array based photovoltaiccells", Appl. Phys. Lett.89 (2006) 023508-1-3.
[19] Green, M. A.; Emery, K.;Hishikawa,Y.; et al,"Solar cell efficiency tables,"ProgPhotoVoltaics, vol. 17,no,l,pp.85-94,2009.
[20] G. Nazmutdinova, S. Sensfuss, M. Schro¨ dner, A. Hinsch, R. Satrawan, D. Gerhard, S. Himmler, P. Wasserscheid, "Quasi-solid state polymer electrolytes for dye-sensitized solar cells: Effect of the electrolyte components variation on the triiodide ion diffusion properties and charge-transfer resistance at platinum electrode", Solid State Ionics 177 (2006) 3141.
[21] D.Maheswari, P. Venkatachalam, R. Elangovan and K. Manoharan, "Formation and characterization o f nanosized tio_2 powder by sol-gel method", International Journal of Nanotechnology and Applications, ISSN 0973-631X Volume 5, Number 2 (2011), pp. 129-136