Synthesis, characterization of TiO$_2$ nano particles for enhancement of electron transport application in DSSC with Cu-BPCA Dye

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ABSTRACT: Dye-sensitized solar cells [DSSCs] have attracted extensive attention due to their potential low cost and high energy efficiency, rendering them one of the most promising system for solar-to-energy conversion. The DSSC efficiency was enhanced by intermixing with the use of TiO$_2$ nanoparticles which provides high surface area for accommodating the light-absorbing sensitizer and also the stable conductor for photo generated electrons. In hydrothermal method, the TiO$_2$ nanoparticles synthesis depends on temperature. TiO$_2$ nano particles diameter depends on different autoclaving temperature. TiO$_2$ nanoparticles have been coated on ITO glasses by screen printing method. In this work, we have synthesized TiO$_2$ nano particles which can provide a fast way for electron transport and reduced trapping of photo injected electrons during the path of back contact. The DSSCs were fabricated using the ruthenium dye and electrolyte (I$_3$/I$_3^-$). The crystalline structure of TiO$_2$ has been characterized by DLS, X-ray diffraction, SEM and TEM. The absorption spectra measured by using UV-Vis spectrometer. The IR spectrum has been recorded to know the peaks of Ti-O-Ti in powder sample. It has been found that the efficiency of DSSC was highly affected by the properties of nano particles.

Keywords: Titanium Dioxide (TiO$_2$), Nanoparticles, Dye, DSSC

1. Introduction

Titanium-Di-Oxide is one of the most attractive material in the field of nanoscience also in nano technology because of the potential application of TiO$_2$ in different processes and it has its extraordinary properties like low cost, high stability, biocompatibility, non-toxicity, high chemical inertness, high refractive index, wide band gap etc. It has been already used in the application of efficient photo catalyst for water purification and degradation of dyes, catalyst support, chemical sensor, optical device, electrochemistry, microelectronics and dye sensitized solar cell etc. The important characteristic which affect the performance of TiO$_2$ are its particle size, crystallinity and morphology etc. It generally shows three crystalline phases as anatase (Tetragonal), rutile (Tetragonal) or brookite (Orthorhombic) and...
due to these it is used for optical device\cite{13}. The photo catalytic activity increased by optimizing the size using various synthesis processes like sol-gel\cite{14,15}, solvothermal\cite{16}, co-precipitation, chemical vapour synthesis\cite{17}, reverse micelle method, liquid phase deposition etc. This above processes are liquid phase process and synthesis can be carried by using liquid titanium like titanium tetrachloride, titanium alkoxide as a precursor. These method of preparations are very challenging because the preparation of the required concertation of the precursor and the molar and P$^\text{H}$ ratio of water with liquid titanium should optimized. Also the use of organic precursor leads to the contaminant of the reaction environment. To avoid the high cost of liquid titanium salt and above reaction conditions, we have used the TiO$_2$ micro particle powder as precursor for the synthesis of the nano sized particles by hydrothermal process.

2. Experimental section

All chemical used in the experiment were analytical grade. Titanium dioxide (TiO$_2$) from (MERCK) has been used for the synthesis.

2.1 Synthesis of TiO$_2$ nano particles

The TiO$_2$ micro particles powder was mixed with 10M NaOH and treated hydrothermally at 150$^\circ$C in an autoclave for 24 hours. After hydrothermal reaction the sample was washed by 0.1M HCl solution to make the sample neutral of P$^\text{H}$ 7. Then the white solid was dried at 80$^\circ$C for 24 hours. After drying the obtained powder was heated at 500$^\circ$C in a hot plate of static air for 2 hours to produce the TiO$_2$ nano particles.

2.2 Preparation of TiO$_2$ slurry and Cu-BPCA dye solution.

The TiO$_2$ slurry was prepared by mixing of 6 ml of ethanol, 3.6 gm of TiO$_2$ nano particles (NPs) and 1 ml of HCl and then stirred for 2 hour with the addition of 0.5-1 ml of deionised water. The dye solution was prepared by mixing Cu-BPCA (dye) with methanol and Poly vinyl alcohol (PVA) for its good adhesive purpose as surfactant.

2.3 Preparation of DSSC device

a) Deposition of TiO$_2$ film

We have identified the conducting side of a tin oxide-coated piece of glass by using a multimeter to measure the resistance. The conducting side have a resistance of 20-30 ohms. With the conducting side up, taped the glass on three sides using one thickness of tape. Wiped off any fingerprints or oils using a tissue wet with ethanol. Added some of the
titanium dioxide suspension and quickly spreaded using a glass rod. The tape served as a 40-
50 micrometer spacer to control the thickness of the titanium dioxide layer. Heated the glass
on a hotplate in a hood for 10-20 minutes.

b) Staining TiO₂ with the dye

Immersed the coated glass piece in a solution of Cu-BPCA dye. The white TiO₂ has been
changed color as the dye was absorbed and complexed to the Ti(IV) ensuring the dye bound
to the TiO₂ film. When visible light was absorbed by dye, excited electrons are formed. This
in turn transferred an electron to the TiO₂ which leads to the generation of electricity in the
DSSC.

c) Carbon coating on the counter electrode

To prepare the counter electrode, the second piece of tin oxide glass, putting the conducting
side down, through a candle flame to coat the conducting side with carbon (soot). In between
the two layers, Iodine solution was kept as an electrolyte solution.

2.4 Material characterisation

The characterisation of the synthesized TiO₂ nano particles were carried out by using PXRD
(Shimzdu, Japan), DLS (Malvern, Germany), UV-Visible spectrophotometer (Shimzdu,
Japan) and FT-IR (Thermoscientific, NICOLET iS5 ID3). The photo current production has
been measured by I-V measurement system by using solar simulator instrument.

3. Result and discussion

3.1 PXRD

X-ray diffractometer (Shimatzu-6100) with CuKα, λ = 1.54 Å wavelength has been used to
record the PXRD of the samples. Θ-2Θ scans were carried out from 10° to 80° with scan speed
of 2°/min with incidence angle of 10° and step size of 0.02°. In the figure-1, the PXRD
pattern of the TiO₂ nano particles has been shown. It has been confirmed the image that it is
having the anatase phase with good crystalline nature. The average crystalline size of the
TiO₂ nano particles can be found to be 6-100 nm[s]. The particles are crystalline in nature
with 2θ peaks at 2θ = 24.62 (101), 2θ = 28.90 (110), and 2θ = 48.42 (200). The peaks in the
PXRD patterns can be indexed as anatase phase of TiO₂ and the diffraction data was in good
agreement with JCPDS files # 751816.

Crystallite size was obtained by Debye-Scherrer’s formula given by equation
D=K\lambda / (\beta \cos \theta )

Where D is the crystal size; \lambda is the wavelength of the X-ray radiation (\lambda=0.15406 \text{ nm}) for CuKa; K is usually taken as 0.89; and \beta is the line width at half-maximum height. The crystallite size obtained using this formula is 2.3 \text{ nm}^{[19]}.

3.2 UV-Visible spectroscopy

The band gap of TiO_2 nano particles were calculated from the UV-Vis spectra which is shown in Fig.1(b).

Figure-1: (a) PXRD plot of TiO_2 nanoparticle

Figure-1: (b) UV-Visible spectra of TiO_2 nano particles
We got the absorbance at 350 nm and the band gap is found as 3.5 ev. It has been concluded from the UV absorbance spectra that TiO$_2$ reacts with intense UV light and instantly act as a photo catalyst through its hydroxyl radical causing breaking of strong covalent bonds [20].

3.3 FT-IR

![Figure-1: (c) FT-IR (d) DLS of TiO$_2$ nano particles.](image)

The absorption spectra in the infrared region was acquired by using Thermo Scientific Nicolet iS5 spectrophotometer equipped with an ATR accessory with a resolution of 4 cm$^{-1}$ in the range of 400-4000 cm$^{-1}$. The peaks at 3400 and 1650 cm$^{-1}$ in the spectra are due to the stretching and bending vibration of the –OH group. A small peak at 1450 cm$^{-1}$ shows stretching vibration of Ti-O-Ti [21].

3.4 Dynamic Light Scattering

TiO$_2$ nano particles were characterised for its distribution of sizes in 0.1 % w/v TiO$_2$ NPs sample dispersed in 10 mM NaCl by using Zeta Sizer Nano ZS at 25°C. The particle size distribution has been obtained from Malvern, Germany dynamic light scattering instrument. The z-average diameter was measured 421.1 nm. Some of the particles are in the size of 108.2 nm which was much smaller than the expected sizes [22].
Photoluminescence spectra of TiO$_2$ nano particles were recorded in an excitation frequency of 479 nm and at room temperature.

![Graph](image)
The photoluminescence spectra in anatase TiO₂ form has been shown in Fig.1(e), which is originated due to self trapped excitons, surface state and oxygen vacancies. The oxygen vacancy peak normally shows at a range of 391 nm to 409 nm. In our sample it showed in these ranges which indicated the photoluminescence emissions happened due to the vacancy of oxygen in the TiO₂ nano particles.

### 3.6 Transmission Electron Microscopy & Scanning Electron Microscopy

**Figure-1:** (f) TEM (g) SEM of TiO₂ nano particles

TEM images of hydrothermal derived nanoparticles are shown in Fig. a. Clear rod shape structures can be seen in the Fig. a having diameter 6 ~ 100 nm. Selected area diffraction is shown in inset of Fig. Which clearly indicates that the TiO₂ nanoparticles are highly crystalline in nature. As can be seen from the TEM image that the average particle size is ~ 20 nm, which is in agreement with the crystallite, size obtained from XRD. The SEM images in fig-b shows particles with great aggregation. The shape of the particle is not uniform and it looks like spherical in shape.

### 3.7 Band gap of TiO₂ nanoparticles

The band gap is found as 3.5 eV. It has been concluded from the UV absorbance spectra that TiO₂ reacts with intense UV light and instantly act as a photo catalyst through its hydroxyl radical causing breaking of strong covalent bonds.
3.8 I-V Characterization

The current - voltage characteristic were performed using the instrument Keithley model 2611 source measuring unit. We have calculated the I-V Characteristics in dark condition.
From the Fig. 1(i), it has been seen that an ideal diode characteristic has been shown by the device. The Knee Voltage ($V_k$) is found to be approximately 0.9 V \[26\].

4. Conclusion:

$\text{TiO}_2$ nanoparticles have been successfully synthesized adopting a clean and economical synthesis protocol, i.e., hydrothermal method. The formation of the $\text{TiO}_2$ nanoparticles has been confirmed by powder X-ray diffraction (PXRD). The size and morphology of the samples were characterized using scanning and transmission electron microscopy (SEM and TEM). The irregular spherical shaped particles were confirmed through the SEM analysis. The transmission electron microscopic analysis confirms the synthesized $\text{TiO}_2$ nanoparticles with the particle sizes in the range of 6-20 nm having nano rod shapes. The DSSC device was showing an ideal diode characteristic which is the basic requirement of a solar cell.

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Reference:

1. Khan, M.M.; Ansari, S.A.; Pradhan, D.; Ansari, M.O.; Han, H.D.; Lee, J.; Cho, M.H.; J. Mater. Chem. A, 2014, 2, 637-644
2. Nolan, M.P. N.T.; Pillai, S.C.; Seery, M.K.; Falaras, P.; Kontos, A.G.; Dunlop, P.S.M., Hamilton, J.W.J.; Byrne, J.A.; Sheaf, K.; Entezari, M. H.; Dionysiou, D. D.; Appl. Catal., B, 2012, 125, 331–349.
3. Kavitha, M.; Gopinathan, C.; and Pandi, P.; International Journal of Advancements in Research & Technology, 2013, 2, 4.
4. Ocwelwang, R.A.; Tichagwa.L.; International Journal of Advanced Research in Chemical Science (IJARCS), 2014, 1, 2, 28-37.
5. Khataee, A.R.; Zahraa, P.O.; J. Hazard. Mater., 2009, 168, 1, 451–457.
6. Ba-Abbad, M.M.; Kadhum, A.A.H.; Mohamad, A.B.; Takriff, M.S.; Sopian, K.; Int. J. Electrochem. Sci., 2012, 7, 4871 – 4888.
7. Kulwicki, B.M.; J. Phys. Chem. Solids, 1984, 45, 1015–1031.
8. Micheli, A.L.; Am. Ceram. Soc. Bull. 1984, 63, 694–698.
9. Pal, K.; Majumder, T. P., Neogy, C.; Debnath, S. C., J. Mol. Struct., 2012, 1016, 30–38.
10. Allen N. S.; Edge M.; Verran J.; Stratton J.; Maltby J.; Bygott C.; Polym. Degrad. Stab., 2008, 93, 1632-1446.
11. Wang Y.; Wu J. H.; Lan Z.; Xiao, Y.; Li, Q.; Peng, F.; Lin, J.; Huang, M.; Chinese Sci Bull, 2011, 56, 2649-2653.
12. Monticone, S.; Tufeu, R.; Kanaev, A.V.; Scolan, E.; Sanchez, C.; Appl. Surf. Sci. 2000, 162, 565–570.
13. Thamaphat, K.; Limsuwan, P.; Ngotawornchai, B.; Nat. Sci., 2008, 42, 357 – 361.
14. Hema, M.; Arasi, A.Y.; Lselvi, P. T.; Anbarasan, R.; Chem Sci Trans., 2013, 2, 239-245.
15. Lee, C.H.; Rhee, S.W.; Choi, H.W.; Nanoscale Res. Lett. 2012, 7, 48
16. Marco, L.D.; Manca, M.; Giannuzzi, R.; Malara, F.; Melcarne, G.; Ciccarella, G.; Zam, I.; Cingolani, R.; Gigli, G.; J. Phys. Chem. C, 2010, 114, 4228–4236.
17. Djenadic, R.; and Winterer, M.; Nano Science and Technology, 2012, 49-76.
18. Sagadevan, S.; Am. J. Nanosci. Nanotechnol. 2013, 1, 27-30
19. Vijayalakshmi, R.; Rajendran, V.; Arch. Appl. Sci. Res., 2012, 4, 1183-1190.
20. Jwo, C.S.; Tien D.C.; Teng T.P.; Chang H.; Tsung T.T.; Liao C.Y.; Lin, C. H.; Rev. Adv. Mater. Sci. 2005, 10, 283-288.
21. Thangavelu, K.; Annamalai, R.; Arulnandhi, D.; IJETAE, 2013, 3.
22. Piskin, S.; Palantöken, A.; Yilmaz M.S.; International Conference on Emerging Trends in Engineering and Technology (ICETET'2013), 2013, 7-8, Patong Beach, Phuket (Thailand)
23. Saraf, L. V.; Patil, S. I., Ogale, S. B.; Int. J. Mod. Phys. B, 1998, 12, 2635-2647.
24. Ho, C.Y.; Lin, J. K.; Wang, H.W.; Solid State Commun., 1993, 87, 847-850.
25. Razali, M.H.; M. N, A.F.; Sreekantan, S.; Mohamed, A.R.; Adv. Mater. Res., 2013, 772, 365–370.
26. Merlino, R. L.; Am. J. Phys. 2007, 75, 1078-1085.