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XRD and SEM Analysis, and Semiconductor Type Determination of TiO_2 for Dye-sensitized Solar Cell

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Abstract— *Titanium dioxide (TiO_2) is a wide band-gap n-type semiconductor. Anatase TiO_2 is the most common structure used in high performance dye-sensitized solar cell (DSSC). Nanoporous TiO_2 serves double-duty as an electron acceptor and a scaffold to hold large numbers of dye molecules in DSSC. The porosity of TiO_2 is a key feature as it has roughly a thousand times greater a surface area than the equivalent flat area. In this work, TiO_2 crystallite size (43.55 nm) has been calculated by using XRD data, and the morphology and the grain-size of TiO_2 (average grain size of 0.2 μm ~ 0.3 μm) with different solvents have been also studied by SEM.*

Index Terms— *Anatase, DSSC, SEM, TCO, TiO_2, XRD.*

I. Introduction

Large amount of carbon dioxide emission by the combustion of fossil fuel leads to serious environmental problem such as the global warming. Solar energy is regarded as one of the perfect clean energy resources. Because the amount of solar energy reaching the surface of the earth is about 10,000 times larger than worldwide energy consumption. So, there would be no worry for the energy supply line even if a small fraction of sunlight could be converted to alternative and usable energy forms.

Devices that will permit direct conversion of sunlight to electricity are called photovoltaic solar cells. But the price of the first and second generation photovoltaic cells exceeds that from the traditional fossil fuel. So, dye-sensitized solar cell (DSSC) has been regarded as the most prospective clean energy source. DSSC consists of four main parts such as TiO_2 (electron acceptor), dye sensitizer (photochemical pumping device), redox electrolyte (electron donor) and carbon layer (catalyst)[1][3][5-7].

Titanium dioxide (TiO_2) is cheap, abundant, nontoxic and biocompatible, and anatase TiO_2 is the low temperature stable form and it gives mesoscopic films that are transparent and colorless[11]. DSSCs are able to work under cloudy skies and non-direct sunlight, and also used indoor. Dr. blade technique, screen printing, spin coating, spray pyrolysis, electrochemical deposition and gas phase deposition can be used to deposit TiO_2 colloidal on transparent conducting oxide (TCO) layer of glass electrode. Nanoporous TiO_2 used in this work, has double-duty: (i) a scaffold to hold large numbers of dye molecules and (ii) an electron acceptor. ZnO, Fe_2O_3, SnO_2, CdSe, CdS, etc can be used as electron acceptor in DSSC[4][11][12].

X-ray diffractometry is mainly used for the identification and qualification of the samples by their diffraction patterns. The sample is placed in the centre of goniometer. After that it is scanned through an angle 2θ from 10^o to 70^o and the diffracted X-rays enter the detector, and then the data are recorded. These data produce their respective diffraction patterns which are identified by JCPDS (Joint Committee on Powder Diffraction Standards) files. So, XRD is a useful technique to investigate the crystal structure, the Miller indices (h k l) and the lattice parameters (a, b, c) of the sample studied. By using the Miller indices and the lattice parameters, the interplannar spacing can be evaluated and then the crystallite size can also be calculated by Scherrer formula[2][9].

Scanning Electron Microscope (SEM) is one of the most versatile instruments available for the examination and the analysis of the microstructural characteristics of solid objects. This is because it can provide high resolution image of the material. Sharply focused high-energy electrons scan over the surface of specimens, and signals can be classed as secondary electrons, backscattered electrons, characteristic X-rays, and auger electrons. Photographic images of various energies can be obtained. SEM can be directly used to observe the surface micro-structures. Its magnifications are from 10 to 200000 or more[8]. Fig 1.1 shows the structure of TiO_2 based DSSC.

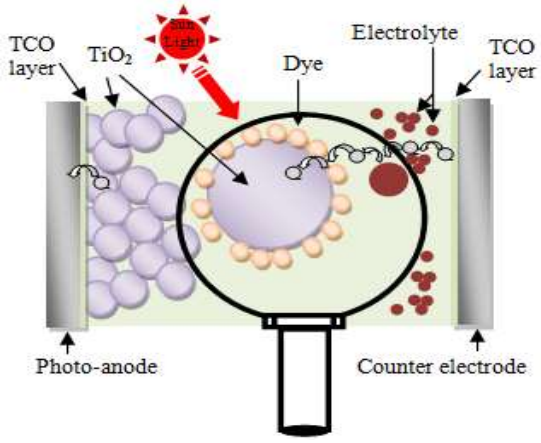

Fig. 1.1 Structure of TiO2 based dye-sensitized solar cell

II. Background Theory

2.1. X-ray Diffractometry (XRD)

XRD can be used to investigate the crystal structure of the sample studied. By using the following formula, the interplannar spacing can be evaluated for tetragonal structure.

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$$\frac{1}{d^2}=\left[\frac{h^2+k^2}{a^2}\right]+\frac{l^2}{c^2}$$

where d = interplannar spacing
a, c = lattice parameters
(h k l) = Miller indices

This is Bragg's law formula. Bragg's law action is shown in Fig 2.1.

$$2d\sin\theta = n\lambda$$

where n = 1
d = interplannar spacing
θ = diffraction angle of the peak
λ = wavelength of incident X-ray

The lattice parameters a and c for tetragonal structure can be calculated by

$$\frac{\sin^2\theta}{c^2(h^2+k^2)+a^2l^2}=\frac{\lambda^2}{4a^2c^2}$$

where λ = wavelength of incident X-ray
θ = diffraction angle of the peak

X-ray diffractometer used in this work with the wavelength of 1.54056 Å of copper target, is shown in Fig 2.2[2].

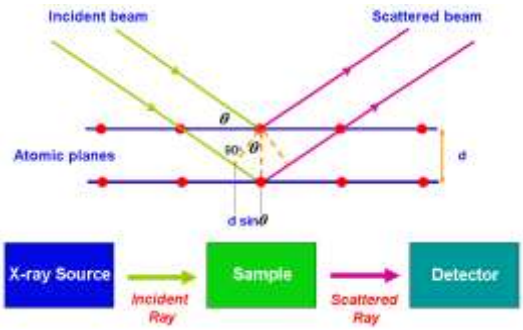

Fig. 2.1 Bragg's law action


Fig. 2.2 X-ray diffractometer (XRD)

The following is the Scherrer formula used to calculate the crystallite size.

$$t=\frac{0.9\lambda}{B\cos\theta}$$

where t = thickness of the crystallites (nm)
λ = wavelength of incident X-ray (nm)
θ = diffraction angle of the peak under consideration at FWHM (°)
B = observed FWHM (radians)

2.2. Scanning Electron Microscopy (SEM)

SEM is one of the more useful instruments to examine and analyze the microstructure of the materials. In the present work, morphological features of anatase TiO_2 powders were investigated by using JEOL JSM-5610LV SEM with secondary electron imaging (SEI) and backscattered electron imaging (BEI), and 10,000 times of photo-magnification. Schematic diagram and scanning electron microscope (SEM) are shown in Fig 2.3 and Fig 2.4 respectively.

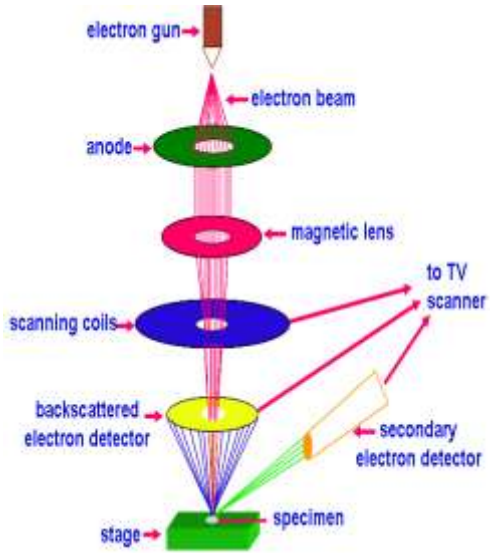

Fig. 2.3 Schematic diagram of SEM


Fig. 2.4 Scanning electron microscope (SEM)

2.3. Semiconductor Type Determination of TiO_2

The hot point probe method has been used to determine the conductivity type of the semiconductor. In semiconductor, there are two types of majority carriers: electron and positive hole. In n-type semiconductor, the majority carrier is electron and hole for p-type. The hot point probe set-up is shown in Fig 2.5. Firstly, the hot soldering gun tip is connected to the positive probe of the multi-meter. The sign of the voltage polarity defines the type of the semiconductor whether n-type or p-type. Due to the hot positive point probe, electrons move away from the hot point and the polarity of the thermal voltage

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shows positive value. Similarly, the majority carriers of p-type semiconductor: holes move away from the point due to the hot point. So, the polarity shows negative.

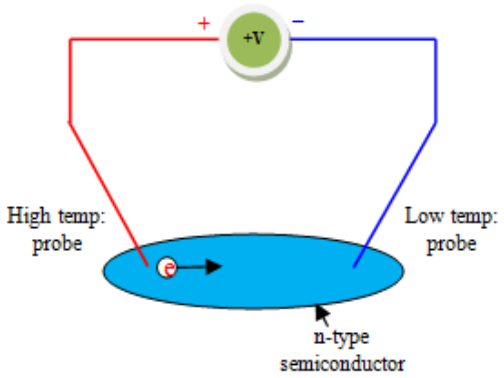

Fig. 2.5 Hot point probe set-up

III. Experimental Details

3.1. XRD Study

Powder X-ray diffraction patterns of TiO_2 is shown in Fig 3.1. XRD data of diffraction angle (2θ), atomic spacing (d), Miller indices (hkl), Full Width at Half Maximum (FWHM) and Peak height (%) of the sample are tabulated in Table 3.1. The collected XRD lines of TiO_2 are (101), (103), (004), (112), (200), (105), (211), (204) and (116). They are found to agree with the standard data of Joint Committee on Powder Diffraction Standards (JCPDS). The appearance of these diffraction peaks demonstrates that TiO_2 possesses tetragonal (anatase), shown in Fig 3.1. The lattice parameters are a = b = 3.7577 Å and c = 9.5227 Å. By using FWHM (B), θ and λ , the crystallite size of TiO_2 can be calculated. But FWHM(B)(degree) needs to be converted into FWHM(B)(radian).

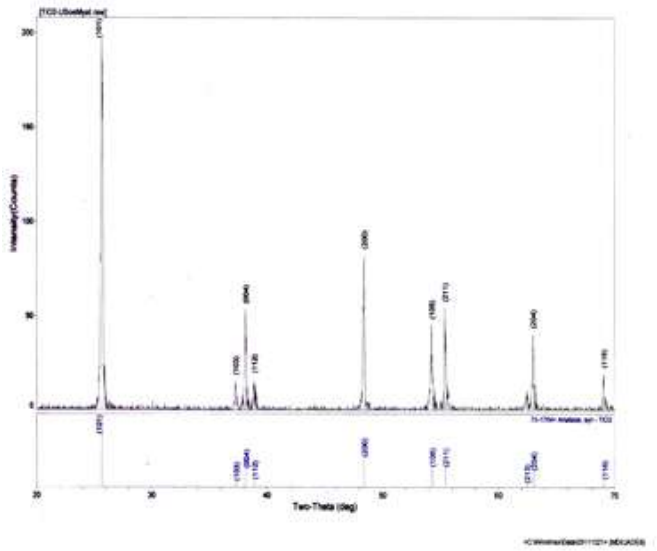

Fig. 3.1 XRD pattern of TiO_2

The crystallite size of TiO_2 is 43.55 nm. The nanoporous structure of TiO_2 layer suggests that the roughness factor of 1000 is achievable while the particle size of TiO_2 is less than 50 nm. In other words, 1 cm^2 coated area of the conductive transparent electrode with nanostructured TiO_2 layer actually possessing a surface area of 1000 cm^2. In this work, the crystallite size of TiO_2 is about 43.55 nm and dye staining area of TiO_2 is about 1000 cm^2.

TABLE 3.1. XRD Data of TiO_2

Line No:	2θ (°)	(hkl)	d (Å)	FWHM (o)	Height (%)
1	25.643	(101)	3.4711	0.185	100.0
2	37.265	(103)	2.4100	0.154	7.6
3	38.140	(004)	2.357	0.157	26.8
4	38.898	(112)	2.3134	0.184	8.1
5	48.397	(200)	1.8792	0.146	41.4
6	54.221	(105)	1.6903	0.159	22.7
7	55.364	(211)	1.6581	0.123	27.3
8	62.986	(204)	1.4745	0.140	20.2
9	69.074	(116)	1.3587	0.136	9.6

3.2. SEM Study

SEM has been employed for the characterization of morphology of TiO_2 powder. Fig 3.2, Fig 3.3 and Fig 3.4 show the SEM images of TiO_2(raw), TiO_2(H_2O_2) and TiO_2(HNO_3) respectively. The porosity of TiO_2 is essential not only to ensure high roughness factor, but also to enhance the penetration of the redox couples into film. According to the SEM images, TiO_2 with HNO_3 has larger porosity than that with H_2O_2. TiO_2 is composed of interconnected spherical shaped particles with an average grain size in the range 0.2 μm ~ 0.3 μm. Most of the TiO_2 powders are uniform with clear grain boundary.

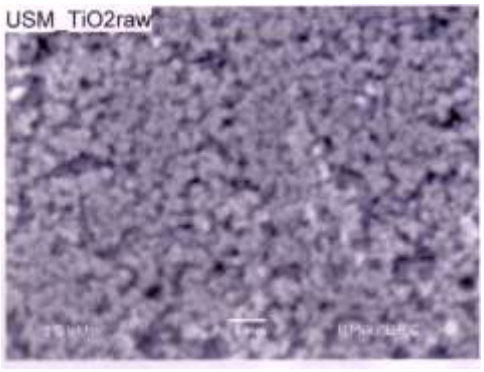

Fig. 3.2 SEM image of TiO_2 (raw)

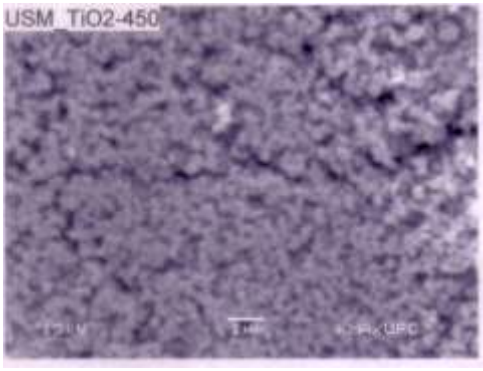

Fig. 3.3 SEM image of TiO_2 (H_2O_2)

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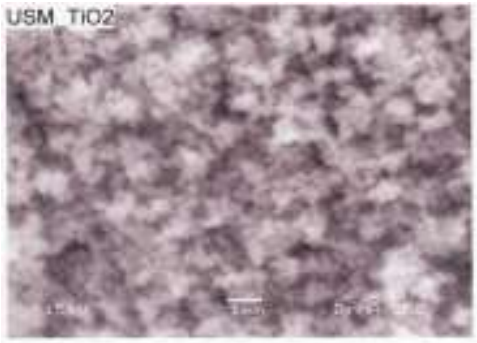

Fig. 3.4 SEM image of TiO_2 (HNO_3)

3.3. n-type Semiconductor TiO_2

According to the literature, TiO_2 is wide band-gap n-type semiconductor with band-gap energy 3.2 eV. So the hot point probe method has been used to determine the type of the semiconductor whether p-type or n-type. On the other hand, the conductivity type (plus or minus) has been studied by the hot point probe method. The hot soldering gun tip is connected to the positive probe of the multi-meter first. And then the measurements can be made as shown in Fig 3.7. The polarity of TiO_2 thermal voltage is positive in Table 3.2. It means that the majority carriers (electrons in n-type) moves away from the point in which the high temperature probe of voltmeter exists and the polarity of the thermal voltage shows positive value. So, TiO_2 in this work is n-type semiconductor.

Fig. 3.8 Positive polarity of TiO_2

TABLE 3.2. n-type semiconductor TiO_2

Sample	Thermal voltage (V_t)	Semiconductor type
TiO_2	+9 mV	n-type semiconductor

IV. Results and Discussion

4.1 XRD and SEM Results

Anatase and rutile are two crystalline forms of TiO_2 (the third form, brookite, is difficult to obtain). From XRD data, TiO_2 is anatase form of tetragonal structure with crystallite size of 43.55 nm and the lattice parameters are a = b = 3.7577Å and c = 9.5227Å. To increase the dye adsorbing area on TiO_2, the crystallite size of TiO_2 needs to be as small as possible. Therefore, P-25 commercial TiO_2 powder should be used to achieve small crystallite size. Moreover, TiO_2 (rutile) has larger crystallite size than anatase. So, TiO_2 (anatase) is suitable to use for the high performance of DSSC. The size of TiO_2 with hydrogen peroxide (H_2O_2) becomes slightly greater than that of TiO_2 with HNO_3 as shown in SEM images. In addition, it was found that TiO_2 layer with H_2O_2 can easily peel off from TCO glass after sintering at 450°C. So, HNO_3 (pH 3-4 in deionized water) should be used as the solvent for TiO_2 suspension. According to the hot point probe method, TiO_2 is n-type semiconductor. So TiO_2 is a wide band-gap n-type semiconductor with cheap, abundant, nontoxic and biocompatible. And then TiO_2 gives transparent and colourless mesoscopic film. So TiO_2 based DSSC can be able to work under cloudy skies and non-direct sunlight, and also used indoor. According to SEM data, the average grain size of TiO_2 is in the range of 0.2 μm ~ 0.3 μm[10]. And then TiO_2 have clear grain boundary and uniform shape.

V. Conclusion

In XRD pattern, (hkl) planes: (101), (103), (004), (112), (200), (105), (211), (204) and (116) show that TiO_2 has tetragonal (anatase) structure. The crystallite size of less than 100 nm is suitable for a scaffold to hold large number of dye molecules.

As shown in SEM images, TiO_2 with solvent HNO_3 has larger porosity than that with solvent H_2O_2. Large porosity gives high roughness factor to stain the large number of dye molecules and to penetrate the redox couples into the film. According to the hot point probe method, positive polarity of TiO_2, in Fig 3.8, shows n-type semiconductor.

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