

Photoelectric Characteristics of Nano TiO<sub>2</sub> Film Prepared By Spraying Pyrolysis Method

Review Article

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## Abstract

The nanocrystalline TiO<sub>2</sub> (nc TiO<sub>2</sub>) film was prepared by spraying pyrolysis method. Starting material for the synthesis was TiCl<sub>4</sub>. Phase compositions and crystalline sizes were examined by pattern of XRD, and surface morphology of the thin film was analyzed by SEM and AFM. Optical characteristics were examined by UV – Vis and luminescent spectra (PL). Electric characteristics were examined by measuring resistance changing of films versus temperature. The experimental data showed that the forming films had nanostructure and typical photoelectric characteristics of nano TiO<sub>2</sub> material which is similar to the ones prepared by other preparing methods. IF compared to others, this preparing method has such as simple equipments, inexpensive and available materials; so it is suitable for mass production.

**Keywords:** Nano TiO<sub>2</sub> film; Spraying Pyrolysis Method.

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## Introduction

Nano titanium oxide has a lot of applications in real life. It is used to make dye in industry to produce paint, plastic, paper and food products. TiO<sub>2</sub> has been even covered on interior furniture to create reflected light effects which increase their beauty, etc. Together with development of nano material technology, at present, there are important applications of nano (nc) TiO<sub>2</sub> including photocatalysis, solar cells, photon and photoelectron devices, etc. With oxidation potential is 3.2 eV, under effect of ultraviolet light (UV), nc TiO<sub>2</sub> can decompose very strong toxic wastes in environment.

TiO<sub>2</sub> was used as an insulating gate on the field effect transistor (FET) [15], to make detectors for measuring nuclear radiations [2], and to make luminescence devices [4]. When doping more appropriate impurities, it will create energy levels of E<sub>a</sub> located in the bandgap. If electrons simultaneously jump from excited levels to elementary energy levels, the material shall generate desired

radiations. The change of color windows act based on this principle. The impurities energy levels can be controlled by electric field; therefore, we have color changing instantaneously depending on the control of the electric field [10, 20]. TiO<sub>2</sub> was also used to make anti reflexing layers help enhancement of efficiency of photoconductor amplifiers (laser) GaInAs/AlGaInAs [12]. Because TiO<sub>2</sub> has very large refractive index, fiber optic cables or optic windows covered this material, which acts based on continuous reflection principle, will produce total reflect, which will minimize the loss of light (sign).

There have been different methods used to prepare nano materials and nano films from relatively simple to rather complex including physics methods (Physical vapor deposition – PVD), chemical methods (Chemical vapor deposition – CVD) and many others such as physics and chemical combined method or combined different methods.

Spraying pyrolysis method (SP) is one of the most simple and economic methods to prepare oxide metals. Using nano TiO<sub>2</sub> films prepared by SP method and using inexpensive materials can enhance applied ability of this material [1]. Besides the simplicity of the method, low cost with a minimum amount of waste, SP process even permits to prepare cover layers with large areas and easily apply for industrial manufacture [8]. This is remarkable advantage of SP method compared to other methods.

SP method has been used by many authors to prepare nano TiO<sub>2</sub> films including single atom films and polyatomic films from different starting salts. Actually, the authors [18] sprayed pyrolytic liquid mixture of titanium and niobium peroxo-hydroxo on quartz substrate to prepare oxygen sensitive sensor. Another authors [5] prepared TiO<sub>2</sub> films and carbon doped TiO<sub>2</sub> powder using starting material was titanium-tetraisopropoxide, the obtained films have anatase single phase structure, the average size of crystalline particles was ~ 160 nm. Additionally, the authors [1] prepared

TiO<sub>2</sub> films on glass substrate using titanium (IV) isobutoxide [Ti ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>O)<sub>4</sub>] as starting material. Also, the authors [19] prepared TiO<sub>2</sub> films on glass substrate using starting material of C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>Ti, the obtained films have the crystalline particle size from 30nm to 50nm. The authors [17] prepared TiO<sub>2</sub> films by starting materials of TiCl<sub>3</sub> solution. The authors [4] prepared TiO<sub>2</sub> films by using titanium diisopropoxide as starting material, the average size of crystalline particles was ~ 210nm.

## Experiments

### Materials

TiCl<sub>4</sub> was prepared into solution with concentrations ranging from 0.025 to 0.15mol/dm<sup>3</sup> (M). The solution was sprayed with atmosphere-pressure 1.5 at. Substrates were made by optical glass with thickness of 1.2mm. Substrate temperatures were studied ranged from 340°C to 460°C.

### Apparatus

X-ray diffraction patterns (XRD) of nanocrystalline TiO<sub>2</sub> films were measured by a D8-AVANCE BRUKER X-ray diffractometer using Cu K $\alpha$  radiation ( $k = 0.1542\text{nm}$ ) with 0.02°/sec scan rate. Field effect scanning electron micrographs (FESEM) were taken with a FESEM HITACHI S4800 field effect scanning electron microscope. Atom force micrographs were taken with a Multimode-VEECO-USA atom force microscope. UV-Vis absorption spectra were measured by a Shimadzu UV-Vis 2540 absorption spectrometer. Luminescence spectra were measured by a FL 3-22 Jobin – Yvon – Spec., USA.

### Apparatus for preparing nano TiO<sub>2</sub> by spraying pyrolysis method

This apparatus are self-prepared. Scheme of nano TiO<sub>2</sub> film preparing system by spraying pyrolysis deposition method was showed in Figure 1. Temperature controlling system used digital technology of OMRON company with degree of displaying accuracy of 1°C. Steam pressure was controlled by two compressed

valves of UniD800 (Taiwan). Spraying frequency was controlled by electronic IC system which may control all of pulse to alter not only spraying time but also pausing time.

## Results and Discussion

### Structure and morphology of nano TiO<sub>2</sub> films

The crystalline phase of ellipsoidal TiO<sub>2</sub> was characterized by X-ray diffractometer. Figure 2 shows the film XRD pattern deposited from spraying pyrolysis deposition method at 380°C with solution concentrate of TiCl<sub>4</sub> = 0.03M. The XRD pattern shows that Bragg reflections were very clear at typical diffraction angles  $2\theta = 25.4^\circ, 38.8^\circ, 48.0^\circ$  and  $55.0^\circ$  corresponding to crystalline planes: (101), (112), (200) and (211), they were the same as results of the authors [11]. All of the films had single phase anatase structure.

Figure 3 shows the XRD patterns of the films prepared at different substrate temperatures at the same experimental condition. The XRD patterns showed that at the studying temperature range of 340 – 460°C, all of the formed films had single phase anatase structure.

The surface morphologies of the film deposited at 450°C are shown in Figure. 3 and 4. From the profiles, it can be observed that the film is porous nanostructure with the average grain size of about 20nm. This relates to evaporation process of solvent and semi-finished product in the pyrolysis process from starting material. Image of Scanning electron micrograph (SEM) of the typical pattern prepared by solution concentrate 0.1 M and at temperature of 450°C is shown in Figure. 4 and its atomic force micrograph (AFM) are shown in Figure 5.

The SEM shows the particles are distributed relatively homogeneously and mesoporously. This result agrees with the SEM of nano TiO<sub>2</sub> film of authors prepared by different methods [6, 7].

The AFM image shows that size of crystalline particles obtained in this work relatively uniform at the range ~ 10 – 15 nm, roughness of film was about 100nm, there were a lot of holes inside

Figure 1. Scheme of nano TiO<sub>2</sub> film prepared system by spraying pyrolysis method.

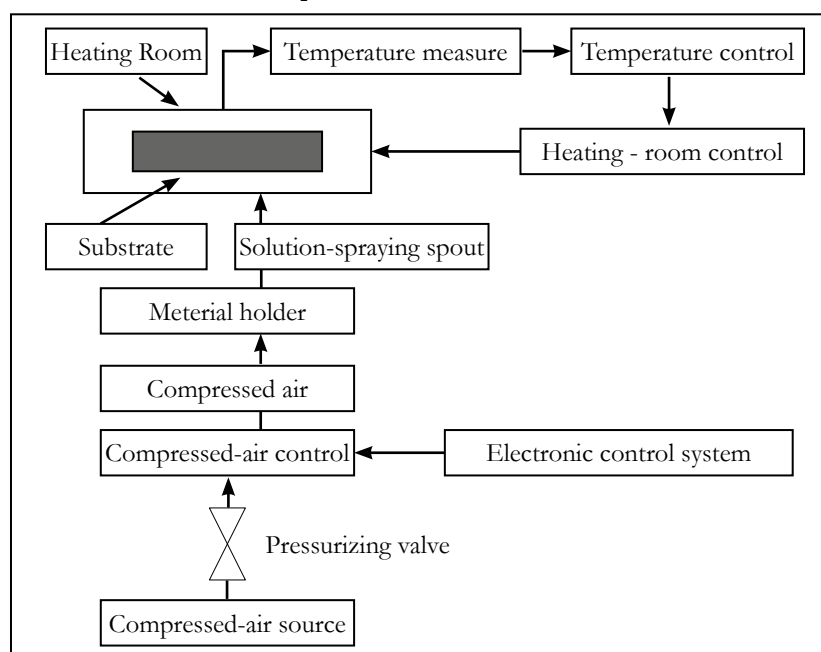


Figure 2. The XRD pattern of TiO<sub>2</sub> film prepared from spraying pyrolysis deposition method at 380°C.

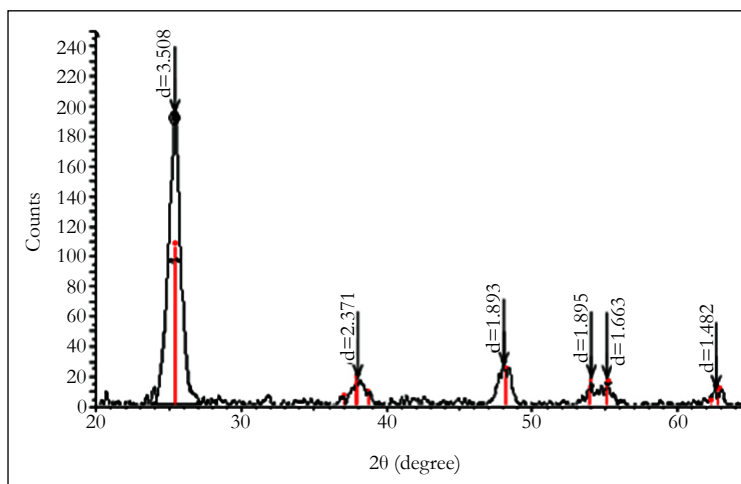


Figure 3. The XRD patterns of TiO<sub>2</sub> films prepared from spraying pyrolysis deposition method at different substrate temperatures

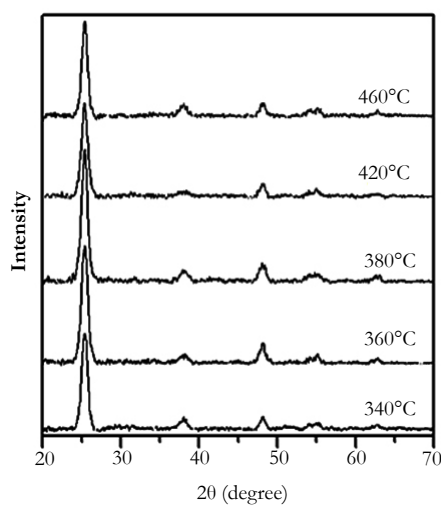


Figure 4. SEM image of nano TiO<sub>2</sub> film deposited from spraying pyrolysis deposition method at substrate temperature of 450°C

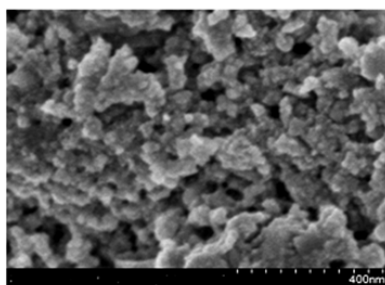
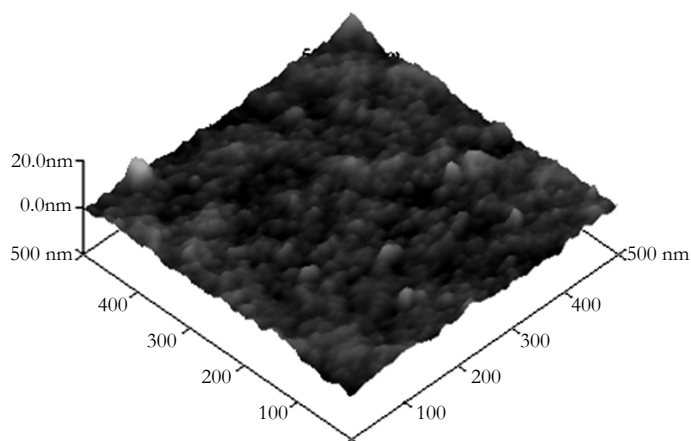


Figure 5. AFM image of nano TiO<sub>2</sub> film deposited from spraying pyrolysis deposition method at temperature of 450°C.



the film. Combined with SEM image, it can be seen that sizes of holes varied on a large scale – in range from ~ 20 nm to ~ 200 nm. The formed films had a very porous structure, so they may have high efficiency on applications of photocatalysis and photoelectrochemical dye sensitized solar cells.

### Optical characteristics of nano TiO<sub>2</sub> films

Figure 6 shows the absorption spectrum of nano crystalline TiO<sub>2</sub> films prepared at substrate temperature of 450°C and solution concentration of 0.1M. Absorption of the films was a function of light wavelength, it slowly increased according to decreasing of wavelength in visible light range, but in ultra violet range absorption coefficient increased very fast corresponding with level transitions band – band of electrons from valence band to conduction band of nano TiO<sub>2</sub>. The shape of absorption spectrum obtained here was the same as that of the authors prepared from TiCl<sub>3</sub> by the same SP method [17], or from TiCl<sub>4</sub> and Ti(SO<sub>4</sub>)<sub>2</sub> by other methods [3, 23, 24], or from commercial nano TiO<sub>2</sub> powder by doctor blade method [22], or of nano TiO<sub>2</sub> particles prepared by hydrolysis method TiCl<sub>4</sub> [14].

Absorption edge was determined by linear extrapolation of absorption coefficient  $\alpha$  in absorption range to value 0 as well as the authors made [16]. Obtained result was adsorption edge at 370 nm, corresponding with photon energy at 3.35 eV.

From absorption spectrum, we can calculate bandgap size from expression for fundamental adsorption coefficient:

$$\alpha(h\nu) = A[h\nu - (E_g \pm h\nu_f)]^2 \text{ ----- (1)}$$

Where  $h\nu$  denotes energy of photon,  $E_g$  is bandgap energy of semiconductor,  $h\nu_f$  denotes energy of phonon,  $A$  is constant.

The authors [6, 9, 17, 19, 23] calculated bandgap size for nano TiO<sub>2</sub> according to Tauc model in the range of high absorption coefficient [9] by expression:

$$\alpha = \frac{A(h\nu - E_g)^{n/2}}{h\nu} \text{ ----- (2)}$$

$A$  is constant which is not dependent on energy of photon, but according to the authors [6] then  $A$  is absorption coefficient which is dependent on energy of photon for the case of nano TiO<sub>2</sub>;  $n = 1$  for allowed direct level transitions,  $n = 4$  for allowed indirect level transitions,  $n = 3$  for forbidden indirect optical level transitions.

Graph expresses  $(\alpha h\nu)^{1/2}$  that is calculated according to absorption spectrum of nano TiO<sub>2</sub> film in Figure 7 on photon energy of incident light was showed on figure 6. Bandgap size ~ 3.35 eV was obtained by extrapolating linearly at the absorption range with high photon energy to value  $\alpha = 0$ . This result was in the value range of other authors [3, 23, 24].

Obtained  $E_g$  value was larger than that of anatase TiO<sub>2</sub> bulk (3.2 eV). The cause may not be by nonstoichiometric composition of nano TiO<sub>2</sub> film, since the nonstoichiometric composition leads to decrease in bandgap size. According to [21], a nonstoichiometry only leads to creating oxygen vacancies (Ti<sup>3+</sup>) acting as trap levels

in TiO<sub>2</sub> layers but does not lead to increasing in bandgap size. This occurs similarly to doped semiconductor. All of the authors reckoned that the increase of bandgap size for nano TiO<sub>2</sub> prepared by different methods with different starting materials was due to quantization of size [14, 16, 22, 23]. The obtained value was in the value range of other authors for nano TiO<sub>2</sub> films prepared by SP method from different starting materials:  $E_g = 3.31 - 3.36$  eV from Titanyl acetylacetonate (TiAcAc) [19]. Direct bandgap size  $E_g = 3.1$  eV from TiCl<sub>3</sub> [17].  $E_g = 2.99; 3.30$  và  $3.32$  eV from solution of ethanol titanium diisopropoxide, corresponding to substrate temperatures were 250, 400 and 500°C [3].  $E_g \sim 3.8$  eV from titanium (IV) isobutoxide [1]. Indirect optical bandgap size  $E_g = 3.39 - 3.42$  eV and direct optical bandgap size  $E_g = 3.67 - 3.72$  eV [9].

Figure 8 shows luminescent spectrum of nano TiO<sub>2</sub> film was excited at wavelength of 330nm. Luminescent spectrum had maximum peak at wavelength of 394.5nm.

In nano TiO<sub>2</sub> material system, luminescent level transitions were band–band level transitions, band–dopant and exciton recombinations. The peaks on luminescent spectrum corresponded with optical level transitions. Maximum of luminescent spectrum stretched in large range may be due to the overlapping spectrum peaks. Luminescent spectrum of anatase nano TiO<sub>2</sub> patterns was thought to belong to exciton traps, oxygen vacant and surface states [13].

UV-Vis adsorption and luminescent spectra of nano TiO<sub>2</sub> film here had the same shape as nano TiO<sub>2</sub> films prepared by other methods [16, 23, 24].

### Electric characteristics of nano TiO<sub>2</sub> films

To study electric characteristics of obtained films, the change of film resistance versus temperature was measured. Studying -temperature range is from room temperature to 450°C. At room temperature, the film was almost insulated. From about 150°C, the film started electric-conducting and then its resistance gradually decreased with temperature increase. This is a typical rule of semiconductor materials. This change rule is shown in Figure 9. From the graph of  $\ln(1/R)$  versus temperature inverse, here  $R$  is resistance of film, we can determine two energy levels:

– At high temperature range, conductivity of film increased due to only heat excitations to jump electrons from valence band to conduction band – this is a range relating to intrinsic conductivity of semiconductor – has value of ~3.32 eV, corresponding with bandgap energy of nano TiO<sub>2</sub>. This result was relevant to the calculated results  $E_g$  from UV–Vis absorption spectrum measurement (~ 3.35 eV).

– At low temperature range, conductivity of film was mainly because carriers were created from dopants ionized – this was a range of conductivity as dopants for extrinsic semiconductor – had value of ~ 0.69 eV, corresponding with dopant level, it may be due to unexpected dopants. This was deep level so it had large carrier catching cross-section. These deep centres relate to luminescent process of TiO<sub>2</sub>, because deep centres usually act as recombinations or effective traps and control life-time of carriers.

Figure 6. UV-Vis absorption spectra of nano TiO<sub>2</sub> film prepared at 450°C.

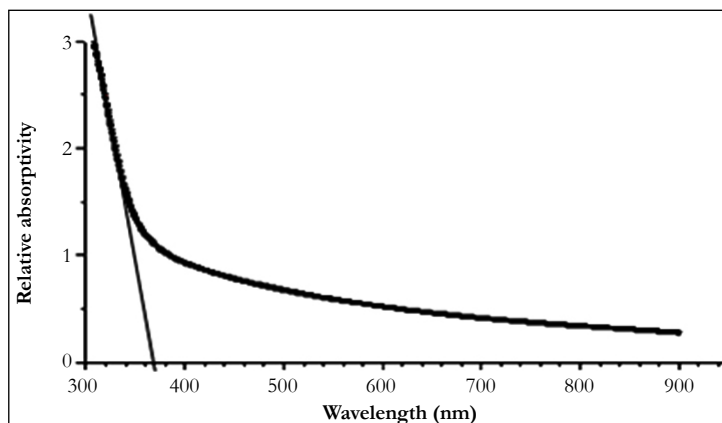


Figure 7.  $(\alpha h\nu)^{1/2}$  as a function of  $h\nu$  for the TiO<sub>2</sub> film calculated according to absorption spectra of nano TiO<sub>2</sub> in figure 6.

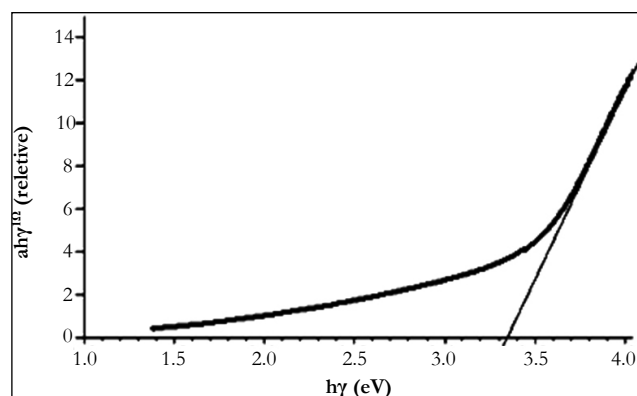


Figure 8. Luminescent spectrum of nano TiO<sub>2</sub> film excited at wavelength 330nm.

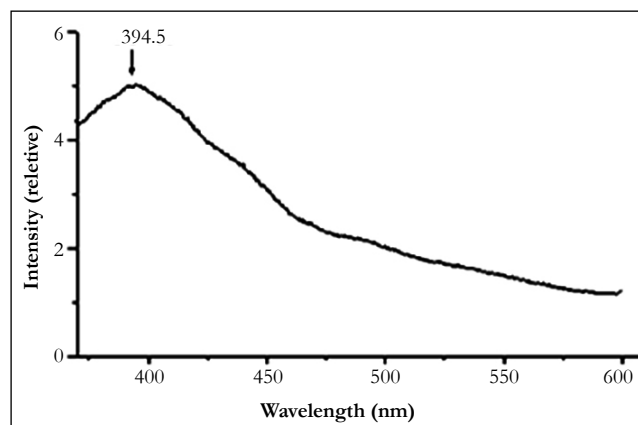
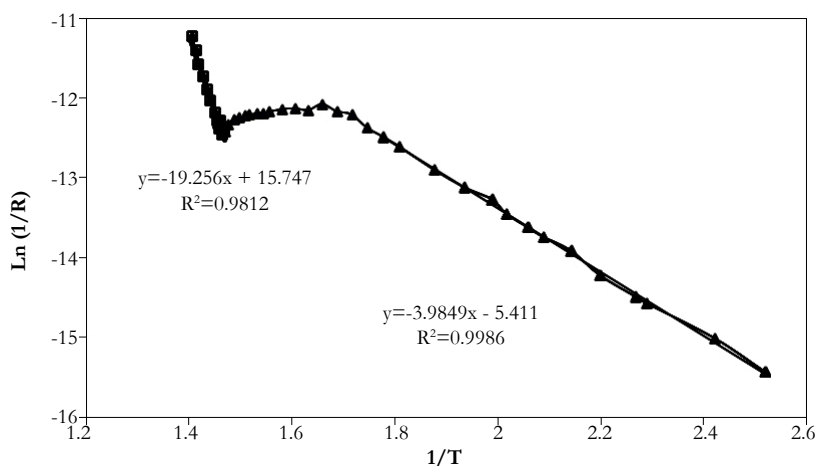


Figure 9. The dependence of resistance of nano TiO<sub>2</sub> film on temperature.





## Conclusion

Nanocrystalline TiO<sub>2</sub> films were prepared by spraying pyrolysis method. Experimental results show that at substrate temperature ranging from 340°C to 460°C with solution concentration from 0.025 to 0.15M, all of them gave TiO<sub>2</sub> films condensed on glass substrate. These were anatase single phase, nanocrystalline TiO<sub>2</sub> films with high crystalline quality and cleanliness, equivalent to other expensive prepared methods include comparison with commercial products. The films had mesoporous structure with average sizes of crystalline particles were at range 7–10nm which were lightly dependent on starting-solution concentration and prepared temperature. This method gave nano TiO<sub>2</sub> films with small particle size and high stability in comparison with other methods.

Characteristic studying results showed that the obtained nano TiO<sub>2</sub> films sufficiently exposed typical photoelectric characteristics of TiO<sub>2</sub> semiconductor material. Characteristic parameters such as absorption spectrum, luminescent spectrum, bandgap size were suitable and equivalent to data of other authors.

Therefore spraying pyrolysis method with simple equipments, used inexpensive and available materials enables to prepare nano TiO<sub>2</sub> films with high quality to meet demands of fundamental and applied researches. This method is able to apply in industrial production.

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