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Simple Hydrothermal Preparation and Dye-Sensitized Solar Cells Efficiency of Nanotubes-Nanoparticles from Thai Leucoexene Mineral

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Abstract— Titanate and TiO_2 have been widely used for energy and environment applications such as a semiconductor in dye-sensitized solar cell(DSSCs), water treatment materials, catalysts, gas sensors, and so on. In this study, titanate nanotubes were synthesized via hydrothermal method from Leucoxene in 10M NaOH at 105 °C for 24 h. The shape, size, crystalline structures and specific surface areas of the prepared nanotubes were characterized by Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) surface area measurements. The prepared titanate nanotubes had an average outer diameter of around 8–10 nm and the inner diameter around 3–4 nm, and particles size around 20-50 nm. The BET surface area and pore volume of the prepared titanate nanotubes were about 144.79 m^2/g and 1.0335 cm^3/g, respectively. This preparation method provides a simple route to fabricate nanotubes from low-cost material using autoclave unit (Thai made). The prepared nanotubes could be applied in dye-sensitized solar cell, which had the solar conversion efficiency up to 3.16% when combined commercial nanoparticles TiO_2 (P25) with the prepared titanate nanotubes from Leucoxene mineral.

Keywords— **Nanotubes; Hydrothermal; Titanate; TiO_2**

1. INTRODUCTION

Over the past decades, nanostructure materials derived from TiO_2 have attracted much attention owing to their excellent properties and important applications, including photocatalysis, photovoltaic devices, luminescence, gas sensors, and solar cells. Low dimensional nanostructures materials have shown many advantages[1-2]. In addition, the discovery of carbon nanostructures was important factor that led the researchers to paid attention to research and development of nanostructures material[3]. Therefore, researchs of TiO_2 and titanate nano-level were focused[4-8]. Because of their exellent properties such as high specific surface area, ion-changeable ability, and photocatalytic ability. TiO_2 and titanate have been considered for extensive applications[1-3, 9-11]. In present, the synthesis of the TiO_2 and titanate nanostructure (including nanotube, nanowire and nanofiber) have made from various methods such as sol-gel, electrodeposition, and hydrothermal approachs[12-16].

In this study, we report the synthesis of nanotube from low-cost Leucoxene mineral under hydrothermal conditions in alkaline solution using Teflon-lined stainless steel autoclave(Thai made) and try to apply the prepared material for electrode in DSSCs. This preparation method provides a simple route to fabricate nanotubes-nanoparticles from low-cost material.

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2. EXPERIMENTAL PROCEDURE

2.1 Synthesis

Leucoxene mineral (<250 μm) 16 g was mixed with 10M sodium hydroxide (NaOH) 2000 ml. Then, the solution was stirred at room temperature for 5 min. After kept stirring, the solution was put into a Teflon-lined stainless steel autoclave, that was built at Rajamangala University of Technology Thanyaburi (RMUTT), Thailand (Fig.1) and heated at 105 °C for 24 h with stirring condition. After the autoclave was naturally cooled to room temperature, the obtained product was washed with 0.1M hydrochloric acid (HCl) solution and deionized water until the treated powders became neutral, followed by drying at 100°C for 24 h (Fig. 2).

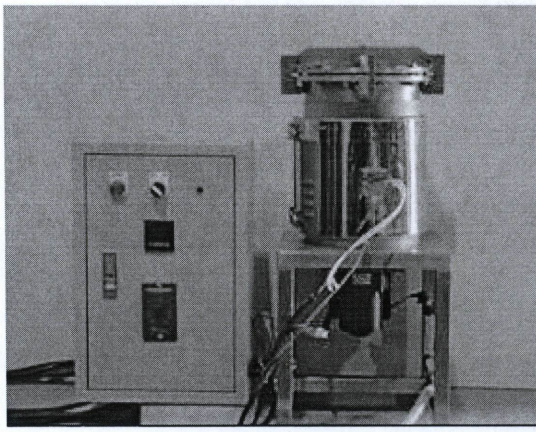

Fig. 1. Teflon-lined stainless steel autoclave unit.

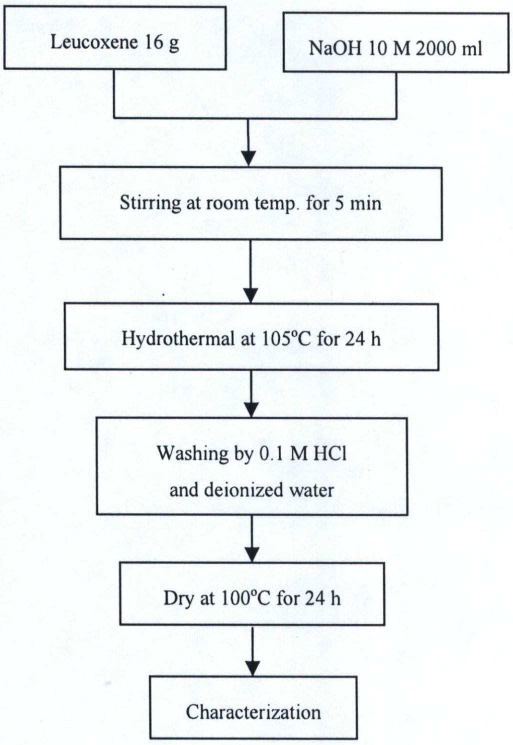

Fig. 2. Schematic representation for experimental procedure.

2.2 Characterizations

The phase identification and crystalline structure of the samples were evaluated by X-ray diffraction (XRD) (X'Pert PRO MPD model pw3040/60, PANalytical). The microstructure of the prepared materials was analyzed by scanning electron microscopy (SEM) (JSM-5800LV, JEOL), and transmission electron microscopy (TEM) (JEM-2100, JEOL). The Brunauer-Emmett-Teller (BET) (BELSORP-Mini, Rubotherm) specific surface area and pore structure of the derived aggregates were characterized determined by the nitrogen adsorption. Photocurrent-voltage curve was measured under simulated solar light (AM 1.5, 100 mW/cm^2).

2.3 Dye-sensitized solar cell measurement

The conducting glass (FTO, TEC 7, Pilkington) was cleaned with DI water and ethanol. Then, nanotubes titanate film were coated on the conducting glass by screen-printing technique and dried it by heat gun. The coating process was repeated to obtain thick films. After coating, the films were burned at 550°C for 1 hour and immersed in 0.3mM of ruthenium(II) dye (known as N719, Solaronix) in a *t*-butanol/acetonitrile (1:1, in vol%). For counter electrode based platform Platinum (Pt) layer was prepared same as nanotubes titanated electrode and were burned at 450°C for 1 hour. Then, the both electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 25 mm thickness made of the ionomer Surlyn 1702 (Dupont). Before measurement, electrolyte (EL-HPE, Dyesol, Australia) was droped into the spaces between cells.

3. RESULTS AND DISCUSSION

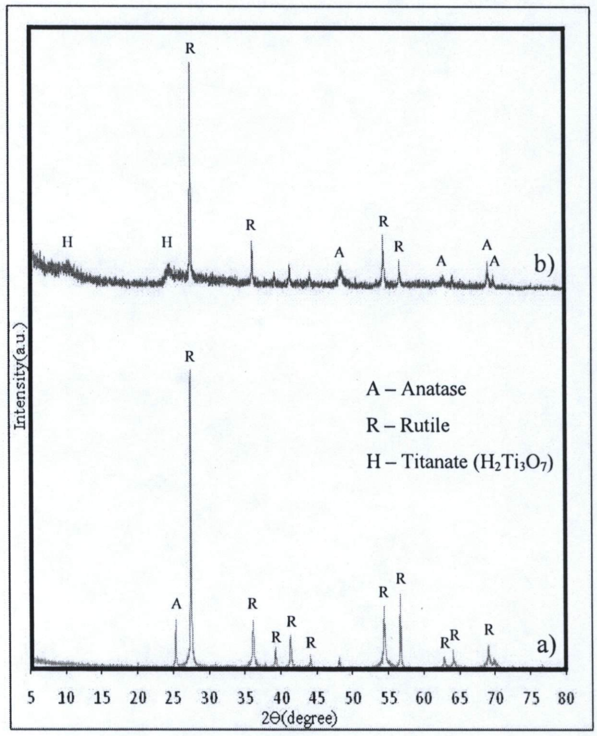

Fig. 3. X-ray diffraction patterns of (a) starting material, (b) the as-synthesized sample.

The XRD peaks of Leucoxene were rather sharp, which indicated the rutile phase(Fig. 3a). After synthesized at 105°C for 24 hour, the sample showed titanate and rutile phase. The XRD peaks of rutile phase after synthersis may be due to the effect of others elements in Leucoxene mineral. The layers of titanate nanotubes are formed depending on the synthesis conditions and residual Na[4,10]. Products could be $H_2Ti_3O_7$ or $Na_xH_{2-x}Ti_3O_7$[4]. The acidic solution is an important factor of the residual Na. The XRD pattern of the as-synthesized sample indicated the crystalline structure of titanate($H_2Ti_3O_7$)[4,10-13] (Fig. 3b) and no crystallization of sodium chloride(NaCl).

In Fig. 4a), shows the SEM image of the Leucoxene with granule diameter about 100-300 μm. The as-synthesized sample shows the tubular shape with inner and outer diameter about 4-6 and 8-10 nm and particles size around 20-50 nm, (Fig. 4b) and 5).

Fig. 6 show the nitrogen adsorption–desorption isotherms and pore size distribution of the prepared sample(as shown in the inset of Fig. 6). From the result, revealed that the prepared sample had an average pore diameter about 3-5 nm. The BET surface area and pore volume of the sample were about 144.79 m^2/g and 1.0335 cm^3/g, respectively. The isotherms exhibit obvious hysteresis loops, an indication of the presence of mesopores (2-50nm) with sharp inflection of nitrogen adsorbed volume at P/P_0 about 1.

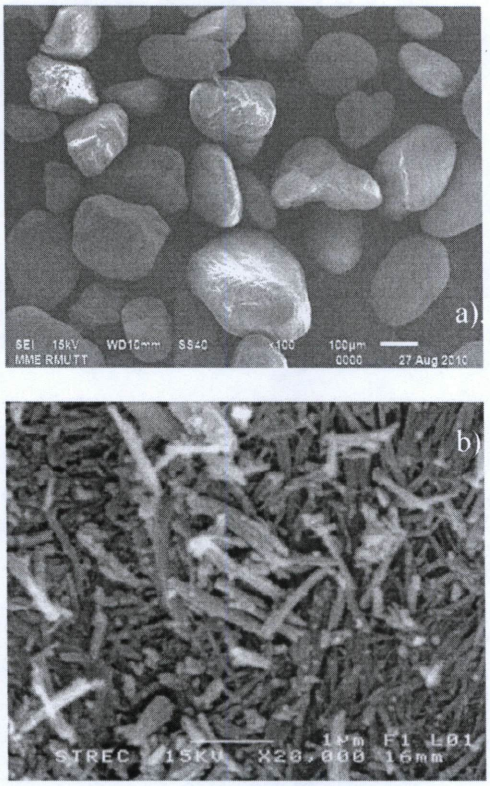

Fig. 4 SEM images of (a) Leucoxene mineral and (b) the as-synthesized sample.

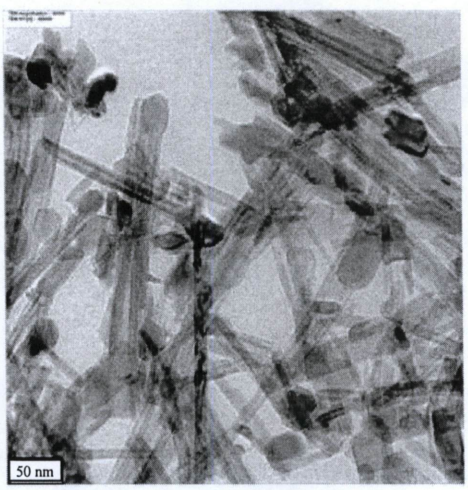

Fig. 5 TEM image of the as-synthesized nanotubes-nanoparticles.

Table 1 BET surface area of samples

Samples	BET surface area (m^2/g)
Leucoxene	~0
Nanotubes/nanoparticles titanate	144.79
Commercial TiO_2 (P25)	~50

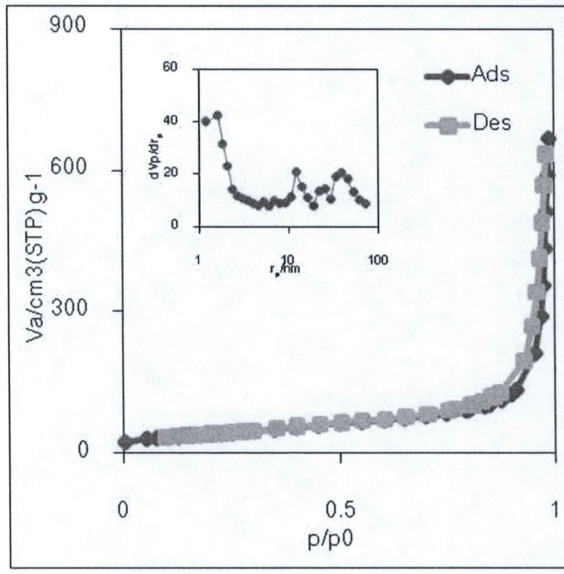

Fig. 6. Nitrogen adsorption isotherm pattern of the as-synthesized nanotubes-nanoparticles.

Interesting, the BET specific surface area of the prepared nanotubes-nanoparticles were about 144.79 m^2/g that greater than starting material (Leucoxene ~0 m^2/g) because of nanotubes-nanoparticles shape [4,10] (Table 1). The conversion efficiency (η) of the cell using nanotubes-nanoparticles combined with commercial TiO_2(P25) was about 3.16 % (Table 2 and Fig. 7), properly, due to the effect of light scattering, electron pathway concept [13-14]. Incorporation of 1D nanostructure and nanoparticle also improved the performance of dye-sensitized solar cells as the recently reported by ref. [17]. Furthermore, the titania film with random packing of one-dimensional fibers-like [17-18] is also expected to enhance the diffusibility of electrolyte in the cell because the porosity and structures of pores are improved from that composed of many very small particles.

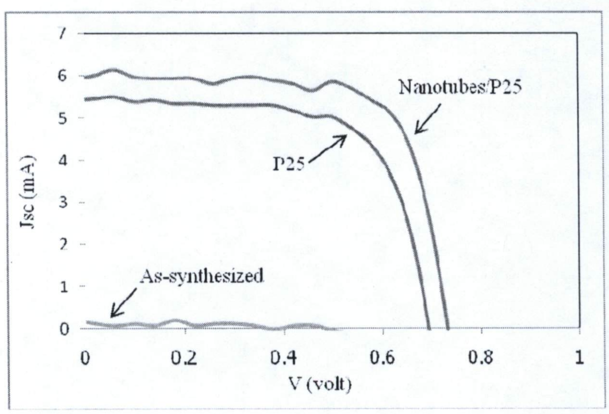

Fig. 7 Photocurrent–voltage characteristic of a typical dye sensitized solar cells fabricated by the as-synthesized sample, the mixed of nanotubes-nanoparticles and P-25 and P-25.

Table 2 Dye-sensitized solar cell efficiency of the cell using nanotubes-nanoparticles combined with commercial TiO_2(P25)

Samples	V_{oc} (V)	J_{sc} (mA/m^2)	FF	η (%)
As-synthesized	0.45	0.14	0.59	0.04
Nanotubes-nanoparticles/P25	0.74	6.01	0.71	3.16
P25	0.68	5.43	0.69	2.56

4. CONCLUSION

In conclusion, nanotubes-nanoparticles were synthesized by hydrothermal method at 105 ° C for 24 hours using Thai Leucoxene mineral as the starting material. The prepared titanate nanotubes had average outer diameter of around 8–10 nm, the inner diameter around 3–4 nm, and particles size around 20-50 nm. The BET surface area of nanotubes-nanoparticles was about 144.79 m^2/g. The conversion efficiency(□) of the cell using nanotubes-nanoparticles combined with commercial TiO_2 (P-25) was about 3.16%.

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