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Fabrication and Utilization of Titania Nanofibers from Natural Leucoxene Mineral in Photovoltaic Applications

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TiO_2 nanofibers were synthesized from natural leucoxene mineral via a hydrothermal process. The shapes, crystalline structure, shape transformation, phase transformation, and specific surface area of the resulting nanostructured materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Brunauer–Emmett–Teller (BET) surface area measurements. The size of prepared nanofibers was about 12–58 nm in width and about 3–22 μm in length. The BET surface area of the prepared sample was about 55 m^2/g. Obtained nanofibers were preliminarily applied as photocatalysts for hydrogen evolution and electrodes for dye-sensitized solar cells (DSSCs).

1. Introduction

Titanate and titanium dioxide (TiO_2)-derived materials have been widely studied and used in various applications, such as semiconductors in dye-sensitized solar cells (DSSCs), water-treatment materials, catalysts, and gas sensors,[1–4] because of their unique characteristics in wide-band-gap semiconductors with many interesting properties, such as high refractive index, low absorption coefficient, and transparency to visible light. TiO_2 is known to exist in three natural polymorphs, i.e., rutile, anatase, and brookite, with different properties. TiO_2 can be synthesized into various nanostructures. Recently, a comprehensive review on the synthesis of titania nanoparticles, nanorods, nanowires, nanotubes, and meso-porous/nanoporous materials by different preparation approaches, such as sol-gel, hydrothermal, solvothermal, and vapor deposition, has become available in the literature.[5)]

Hydrothermal synthesis has become one of the most important and promising fabrication methods for nanomaterials, such as nanoparticles, nanofibers, nanotubes, and nanowires. The fabrication of TiO_2-derived nanowires or nanotubes by treating TiO_2 powder with highly concentrated NaOH have been reported.[6–12] Because of the high cost of TiO_2 powder, the fabrication of nanofibers via a hydrothermal process, in which natural rutile sand was used as a starting material, was investigated.[13,14] The products in those studies were titanate (not TiO_2) nanofibers[13] and TiO_2 (B) nanofibers.[14]

In this contribution, instead of TiO_2 powder or rutile sand, inexpensive-natural leucoxene mineral was used as the starting material for the fabrication of TiO_2 nanofibers by the hydrothermal process with post-heat treatment. The obtained nanofibers were applied as photocatalysts for hydrogen evolution and electrodes for dye-sensitized solar cells (DSSCs).

2. Experimental Procedure

2.1 Synthesis

Nanofibers were synthesized hydrothermally using natural leucoxene sand (Thailand) as the starting material. In a typical synthesis, 16 g of natural leucoxene mineral (without further purification) were put into an autoclave (size = 4 L). Then 2 mL of 10 M NaOH aqueous solution was added into the autoclave and the materials were heated at 120 °C for 72 h with stirring, followed by natural cooling to room temperature. The obtained products were washed with 0.1 M HCl aqueous solution, followed with distilled water several times. Subsequently, the products were freeze-dried. The samples were calcined in air for 2 h at 100–1000 °C.

2.2 Characterizations

The crystalline structure of samples was evaluated using an X-ray diffractometer (XRD; JEOL JDX-3530). The microstructure of the prepared materials was analyzed using a scanning electron microscope (SEM; JEOL JSM 5410) and a transmission electron microscope (TEM; JEOL JEM-2010). The Brunauer–Emmett–Teller (BET) specific surface area was determined from the nitrogen adsorption (Quantachrome Instruments Autosorb-1).

2.3 Investigation of photocatalytic activity for hydrogen evolution

The photocatalytic activity of the nanofibers for hydrogen evolution was investigated by the method reported previously.[15] One gram of sample was suspended in aqueous methanol solution (800 ml water, 80 ml methanol) in an inner-irradiation-type photoreactor made of Pyrex glass. A 450 W high-pressure Hg lamp (Ushio UM-452) was utilized as a light source and cooling water was circulated through a cylindrical Pyrex jacket located around the light source. The hydrogen evolved was analyzed using an on-line gas chromatograph (Shimadzu GC-8A).

2.4 Fabrication of photoelectrode for DSSCs and photovoltaic measurements

A paste of nanofibers was prepared by grinding 1 g of nanofibers with a 5 ml mixture of water/ethanol (1 : 1 v/v) and 0.4 ml of polyoxyethylene (10) octylphenyl ether (Triton X-100). Nanofiber paste was coated on fluorine-doped SnO_2 conducting glass (FTO) by the doctor-blade technique. The film obtained was consequently calcined at 400, 700, or 1,000 °C for 4 h. Calcined electrodes were sensitized by immersing in 0.3 mM ruthenium(II) dye (Solaronix N719) in a mixture of *t*-butanol and acetonitrile. The electrodes were washed with acetonitrile, dried, and used immediately with an iodide–triiodide electrolyte for the measurement

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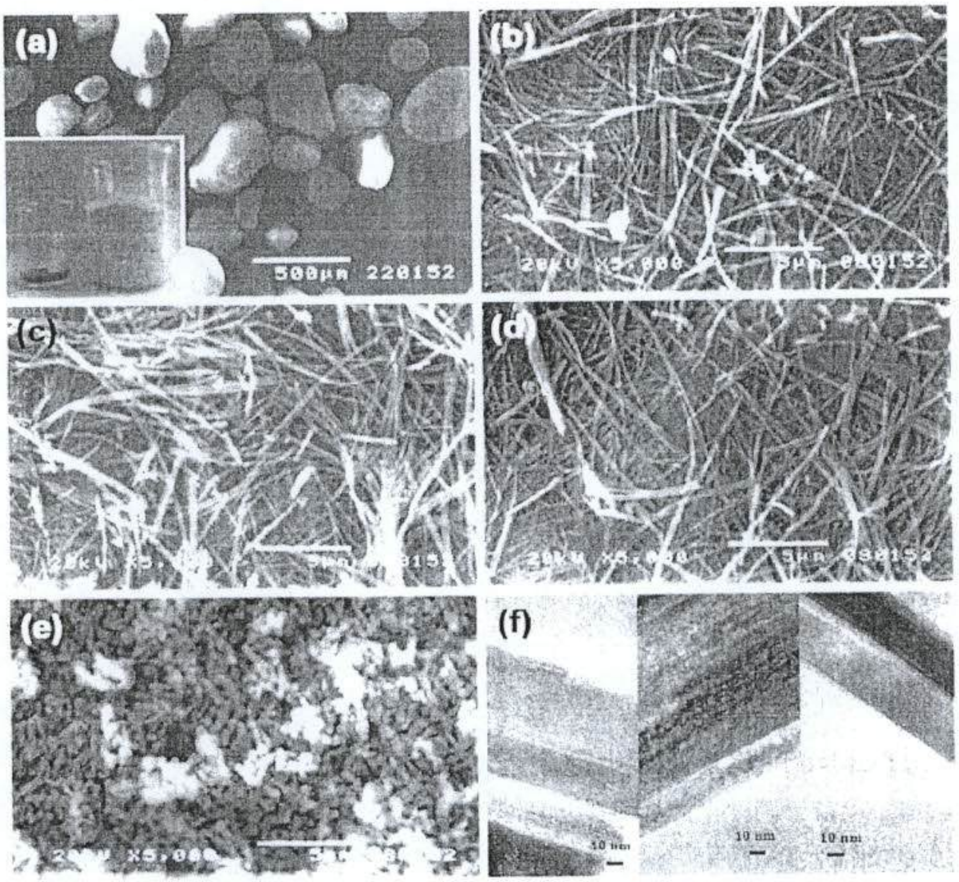

Fig. 1. (Color online) (a–e) SEM images of (a) starting leucoxene sand; (b) as-synthesized nanofibers; and nanofibers calcined for 2 h at (c) 400, (d) 700, and (e) 1000 °C. Inset in (a) is a photograph of natural leucoxene sand (left) and corresponding as-synthesized nanofibers (right). (f) TEM images of as-synthesized nanofibers and nanofibers calcined for 2 h at 400 and 700 °C (left to right, respectively).

of their photovoltaic properties.[16] Photocurrent density–voltage (J–V) curves were measured under simulated solar light (Bunkoh-Keiki CEP-2000, AM 1.5, 100 mW/cm^2).

3. Results and Discussion

3.1 As-synthesized nanofibers

As-synthesized products were yellowish whereas the starting natural leucoxene was dark brown [see inset of Fig. 1(a)]. The volume of as-synthesized products (6.28 g) was much more than that of starting leucoxene (16 g). The components in as-synthesized samples investigated with X-ray fluorescence (XRF) is shown in Table I. The samples were mainly composed of titanium oxide (96.37%) with some impurities.

The SEM image of the starting leucoxene shows the granule size of about 115–358 μm [Fig. 1(a)] whereas the as-synthesized samples showed fiber morphology. The fibers were about 12–58 nm in diameter and 3–22 μm in length [Fig. 1(b)]. TEM images of as-synthesized and calcined nanofibers are shown in Fig. 1(f). The as-synthesized nanofibers were not hollow (not nanotubes). Nanofibers tend to form bundles; thus some of the nanofibers appeared thicker than others. The BET surface area of the as-synthesized nanofibers was 54.92 m^2/g, while that of the starting natural leucoxene sand was very low (near 0 m^2/g) (Fig. 2).

Table I. Chemical components in nanofibers synthesized from leucoxene mineral.

Component	Amount (wt %)
TiO_2	96.37
Fe_2O_3	2.26
SiO_2	0.17
ZrO_2	0.28
Nb_2O_5	0.17
SO_3	0.06
Cl	0.05
CaO	0.08

XRD patterns of leucoxene, as-synthesized nanofibers, and nanofibers calcined at 100–1,000 °C are shown in Fig. 3. The structure of the as-synthesized nanofibers was titanate ($H_2Ti_3O_7$), indicating that there is hydrogen (from water) in the nanofibers.[8,13,17]

3.2 Calcined nanofibers

XRD patterns of the nanofibers calcined for 2 h at 100–400 °C are also shown in Fig. 3(a). In the range of 200–700 °C, the nanofibers were dehydrated and mainly

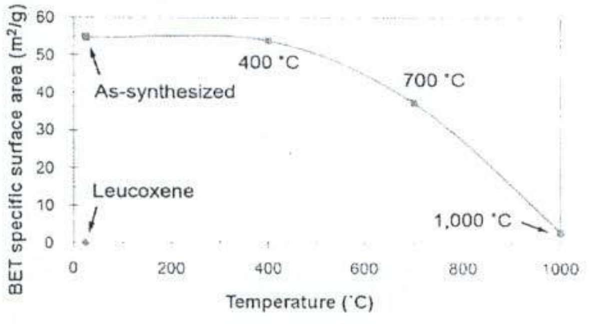

Fig. 2. (Color online) BET specific surface area of starting leucoxene sand, as-synthesized nanofibers, and nanofibers calcined for 2 h at 400, 700, and 1000 °C.

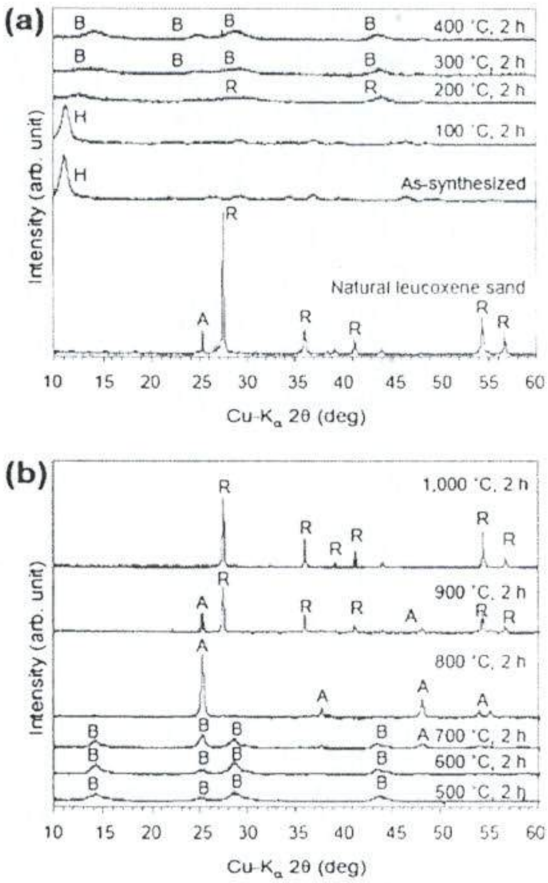

Fig. 3. XRD patterns: (a) starting leucoxene sand, as-synthesized nanofibers, and nanofibers calcined for 4 h at 100–400 °C; and (b) nanofibers calcined for 4 h at 500–1000 °C. A = anatase TiO_2, B = TiO_2 (B), H = hydrogen titanate, and R = rutile TiO_2.

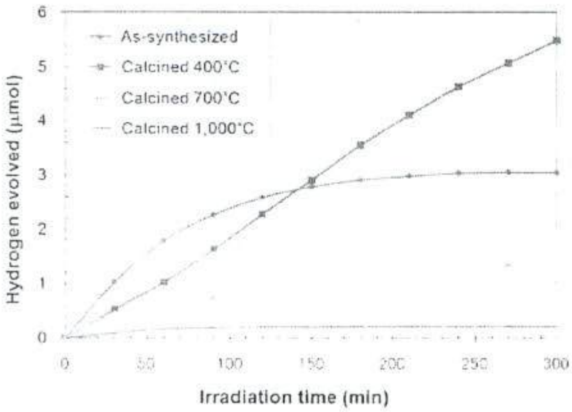

Fig. 4. (Color online) Photocatalytic activity for hydrogen production with nanofibers calcined at various temperatures and for as-synthesized nanofibers.

recrystallized into the metastable form of TiO_2 (B).[10,13] Figures 1(c) and 1(d) show SEM images of the nanofibers calcined for 2 h at 400 and 700 °C, respectively. The nanofibers seem to differ slightly in length. The BET surface area of nanofibers calcined at 400 °C is in the same range as that of the as-synthesized nanofibers. At 700 °C, some crystalline phase was changed to anatase. The crystalline phase was completely changed to anatase above 800 °C. The BET surface area of nanofibers calcined at 700 °C was lower than that of fibers calcined at 400 °C. At 900 °C, the crystalline phase is a mixture of anatase and rutile. The rutile phase was mainly present at 1,000 °C, and at this temperature, nanofibers changed to a nanorod-like structure [Fig. 1(e)]. The BET surface area of the nanofibers calcined at 1000 °C was found to decrease to 3.02 m²/g.

3.3 Photocatalytic activity for hydrogen evolution

The amount of hydrogen evolved from aqueous suspensions containing TiO_2 nanofibers calcined at various temperatures is shown in Fig. 4. It was found that the photocatalytic activity of nanofibers calcined at 400 °C was higher than that of as-synthesized ones, e.g., 5.49 and 3.06 $\mu mol{\cdot}g^{-1}$ after 5 h of irradiation of UV light (based on the amount of 1 g of catalyst), respectively, owing to the crystallinity of the TiO_2 (B) phase of the sample calcined at 400 °C (with same range of surface area). At 700 and 1,000 °C, the nanofiber photocatalyst showed lower activity, i.e., *ca.* 1.46 and 0.22 $\mu mol{\cdot}g^{-1}$ of hydrogen evolved after 5 h irradiation of UV light, respectively. This could be mainly ascribed to the decrease in the BET surface areas and the increase in rutile phase.

3.4 DSSC photovoltaic measurements

The photovoltaic characteristics of DSSCs based on the nanofiber electrode are shown in Table II. For the electrode made from nanofibers calcined at 400 °C, the short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (FF), and the overall conversion efficiency (η) was found to increase as compared with that of as-synthesized nanofibers, because of the higher crystallinity of TiO_2 (B) in the samples calcined at 400 °C. An increase in the calcination temperature resulted in decreases in J_{sc} and η, which corresponds to the case of photocatalyst where an increase in the calcination temperature resulted in a decrease in the amount of hydrogen evolved. The highest η in DSSCs based on the nanofibers synthesized from natural leucoxene was 0.07%, which is significantly lower than that of cells from conventional nanoparticles, e.g., ~6.2% (see Table II). The significant low J_{sc} of DSSCs based on the nanofibers

Table II. Photovoltaic properties of DSSCs made of nanofibers synthesized from leucoxene mineral, nanofibers calcined at various temperatures, and reference TiO_2 nanoparticles (P25) and composite P25/400 °C-calcined nanofibers.

Sample	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
As-synthesized fibers	0.04	0.28	0.24	0.003
Nanofibers calcined at 400 °C	0.19	0.56	0.69	0.074
Nanofibers calcined at 700 °C	0.07	0.35	0.37	0.009
Nanofibers calcined at 1,000 °C	0.05	0.33	0.38	0.006
P25	12.63	0.74	0.67	6.222
P25/400 °C-calcined nanofibers	14.41	0.71	0.68	6.958

synthesized from natural leucoxene may be ascribed to a slightly small number of adsorbed dye molecules on the electrode compared with that of the nanoparticle cell (e.g., 0.17 and 0.56 nmol/cm^2 in 15-µm-thick cells of nanofibers (synthesized from natural leucoxene) and nanoparticles, respectively). The reasons for this result may be the non-anatase TiO_2 samples used in this study and impurities [e.g., Fe_2O_3 (see Table I)] in the fabricated fibers. Even though the photovoltaic performance of nanofibers synthesized from natural leucoxene was not high, the obtained fibers have some advantages, e.g., 1D characteristics (which benefit electron transport), high surface area, and yellowish color (which increases light absorption in the visible range). Therefore, mixing of nanofibers synthesized from natural leucoxene and calcined at 400 °C with nanoparticles (P25) was carried out to fabricate photoelectrodes for DSSCs (nanofibers: P25 = 40 : 60 w/w). The photovoltaic results of the cells are shown in the last row of Table II. At the same thickness of electrodes, the cells made of composite nanofibers/nanoparticles show higher η than those made of only nanoparticles (η of cells comprising composite nanofibers/nanoparticles ~7.0%).

4. Conclusions

TiO_2 nanofibers were synthesized from natural leucoxene mineral via a hydrothermal process. The size of prepared nanofibers was about 12–58 nm in width and about 3–22 µm in length. The BET surface area of the prepared sample was about 55 m^2/g. The morphology, crystalline phase, and surface area of nanofibers could be adjusted by calcination at various temperatures after hydrothermal synthesis. This synthesis method provided a simple route to fabricate TiO_2 nanostructured materials from low-cost materials. The obtained nanofibers were applied as photocatalysts for hydrogen evolution and electrodes in DSSCs. The nanofibers showing the highest photocatalytic activity for hydrogen evolution and highest efficiency in DSSCs were nanofibers calcined at 400 °C, because of their high TiO_2 (B) crystallinity and large surface area.

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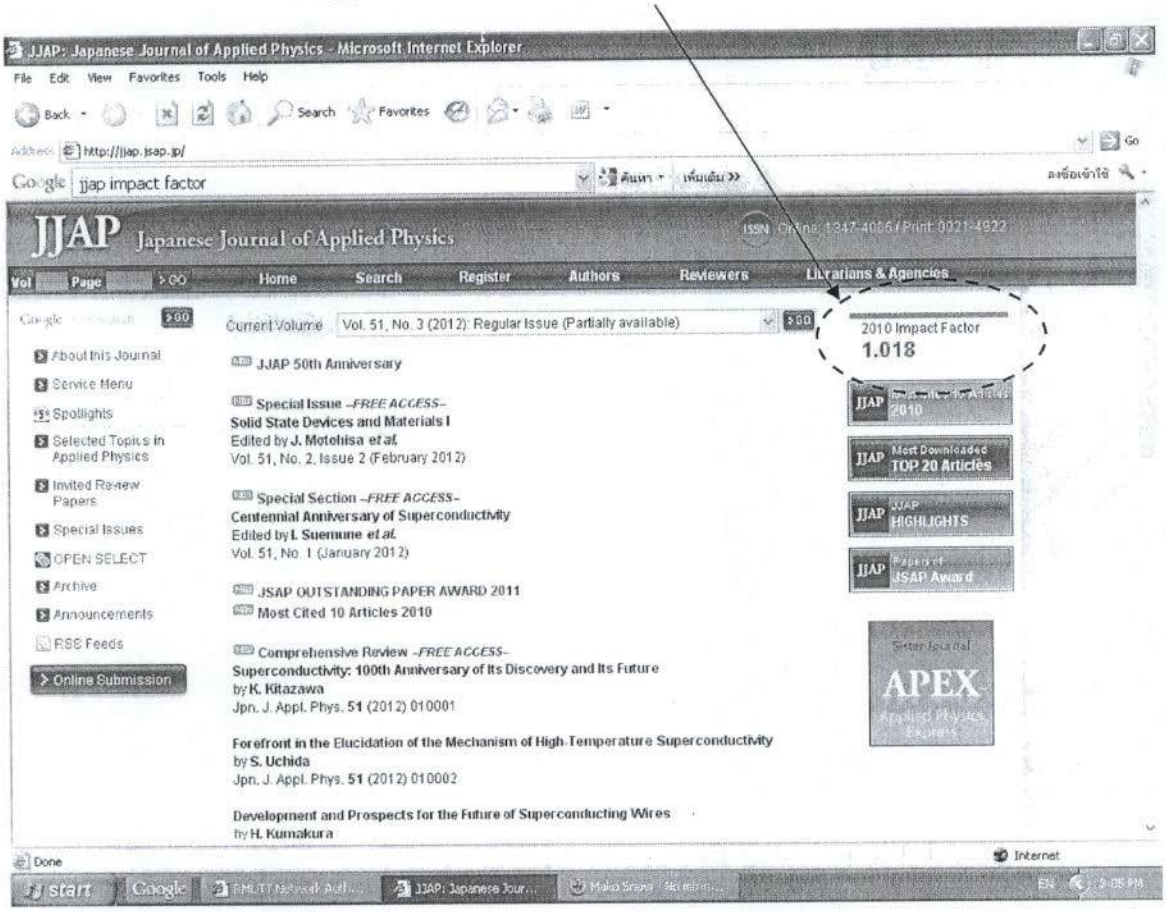

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