

# Photoelectrochemical Activity of Sodium Titanate Nanobelts for Photoanode

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We report photoelectrochemical characteristics of sodium titanate nanobelts as a photoanode. Sodium titanate nanobelts were synthesized by hydrothermal process using titanium(IV) tetrabutoxide in a concentrated aqueous NaOH solution. The formation mechanism of sodium titanate nanobelts in the synthetic process has been comparatively studied on the control of reaction time, pH and concentration of precursors, etc. The morphology and optical property have been investigated with X-ray diffraction, scanning electron microscope, transmission electron microscope, and ultraviolet-visible spectroscopy. On the basis of their morphological and optical characteristics, sodium titanate nanobelts were applied for photoelectrochemical cell as working electrode. After transparent film of sodium titanate nanobelts is formed on the fluorine-doped tin oxide (FTO) glass by doctor blade technique, the photoelectrochemical results were discussed on the structure of photoanode of dye sensitized solar cells.

**Keywords:** DSSC, Sodium Titanate Nanobelts, Photoanode, Hydrothermal Method, Pastes.

## 1. INTRODUCTION

In the past decades, one-dimensional (1D) nanostructures such as nanotubes<sup>1,2</sup> and nanowires,<sup>3,4</sup> have attracted extraordinary attention for their novel physical properties and potential applications in constructing nanoscale electronic and optoelectronic devices. Recently, the discovery of semiconducting oxide nanobelts (ZnO, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, CdO, Ga<sub>2</sub>O<sub>3</sub>, PbO<sub>2</sub>) has initiated great interest in such belt-like nanostructures.<sup>5</sup> There has been much speculation about the properties and potential application of these nanostructures; for example, they were considered as candidates for the fabrication of nanoscale devices. Up to now, considerable efforts have been focused on the synthesis of different compounds with this nanostructure, and several belt-like structures of compounds such as PbO,<sup>6</sup> Si,<sup>7</sup> Zn,<sup>8</sup> and Ge<sub>3</sub>N<sub>4</sub><sup>9</sup> have been reported. As a photocatalyst, these structures are suitable for the accommodation of the catalytic active phases such as noble metal atoms work to enhance the efficiency of the separation of photoexcited charges (i.e., electron and hole) and also for their transfer to adsorbed reactants at the surface.

Thus, it would be expected that these titanates become promising photocatalytic materials.

Among various alkali metal titanate nanomaterials, sodium titanate is one of particular interested materials for its wide applications, such as high photocatalytic activities,<sup>10</sup> ion-exchange ability,<sup>11</sup> and photovoltaic characteristics.<sup>12</sup>

In the study, we employ Na<sub>2</sub>Ti<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> films selected to be as structurally similar as possible and employ it in dye-sensitizing conditions to achieve matched dye loading on each film.

## 2. EXPERIMENTAL DETAILS

### 2.1. Synthesis of Sodium Titanate Nanobelts

Titanium(IV) butoxide (Ti(OBu)<sub>4</sub>, 97+%) and absolute ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH, 99.9%) were obtained from Sigma Aldrich Chemical Co. respectively, and used as received. Titanium(IV) butoxide (Ti(OBu)<sub>4</sub>) was used as Ti precursors and 10 M NaOH aqueous solution was used as the solvent. For sodium titanate nanobelts, 2 mL of Ti(OBu)<sub>4</sub> was added into 20 mL of a C<sub>2</sub>H<sub>5</sub>OH solution and then the solution was mixed with 20 mL of a 10 M aqueous NaOH solution in a teflon vessel and the solution was moved into an autoclave, then heated in a oven at 180 °C for 24 h. The final product was filtered and washed with ethyl alcohol several times and dried at room temperature freely.

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To explore the thermal stability of the crystal structure of the products, the as-synthesized sample has calcinated at 500 °C for 6 h.

## 2.2. Electrodes Fabrication

$\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  nanobelts were placed on the FTO-coated glass by a doctor blade method using Scotch tape as a spacer. The samples were heated in air condition with 500 °C for 30 min.  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  electrodes were soaked in an ethanol solution of 0.3 mM  $(\text{Bu}_4\text{N})_2[\text{Ru}(4,4\text{-dicarboxy-2,2-bipyridine})_2(\text{NCS})_2]$  (“N719” Dyesol, B2) overnight. The samples were then rinsed with ethanol and dried with a  $\text{N}_2$  stream. A 25  $\mu\text{m}$ -thick Surlyn spacer was used to meld the photoanode to a pre-drilled platinumized piece of FTO-coated glass. A solution 0.6 M of butylmethylimidazoliumiodide (TCI America), 0.03 M  $\text{I}_2$ , 0.1 M guanadimium thiocyanate, and 0.5 M 4-tert-butylpyridine in 85:15 acetonitrile/valeronitrile was introduced to the cell by vacuum backfilling through the hole on the dark electrode. A cover glass and a second piece of Surlyn spacer were used to seal the hole on the dark electrode.

## 2.3. Electrode Characterization

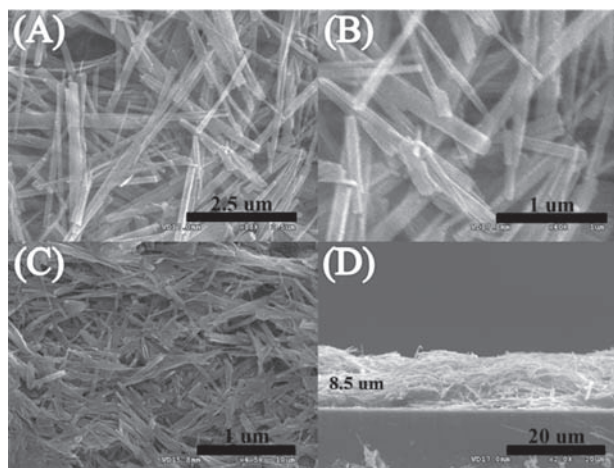
The photoelectrochemical characteristics of  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  electrodes (diameter = 0.7 cm, dimension = 0.38  $\text{cm}^2$ ) as photoanodes were measured using PL-9 potentiostat in a three-electrode cell with 1 M KOH (pH 14.1) as electrolyte using Ag/AgCl in saturated KCl as a reference electrode and Pt wire as a counter electrode. The photoanodes were scanned between 300 and 1000 mV versus Ag/AgCl at a rate of 50 mV/s. The potential-current curves has obtained in 1 M KOH (pH 14.1) under the dark condition and illumination condition. Illumination has performed with simulated sunlight from a 300 W Xenon lamp (Asahi Spectra HAL-320, ozone free) using HAL AM 1.5G filter with a measured intensity of 1 sun (100  $\text{mW cm}^{-2}$ , spectrally corrected) at the sample surface.

## 2.4. Characterization

The crystal structures of the synthesized products were identified by using XRD with a Philips X'Pert-MPD System with a Cu KR radiation source ( $\lambda = 0.154056$  nm). The size and shape of the products were imaged by SEM images (HITACHI H-7500 (low-resolution)). FE-SEM image analysis also has performed by JSM-6700F (JEOL, Japan) for a high resolution. TEM analysis and Energy-Dispersive X-ray (EDX) analysis also has performed with JEOL JEM2010 transmission electron microscope under an acceleration voltage of 200 kV.

## 3. RESULTS AND DISCUSSION

Figures 1(A) and (B) are SEM images of the synthesized sodium titanate nanobelts with low and high

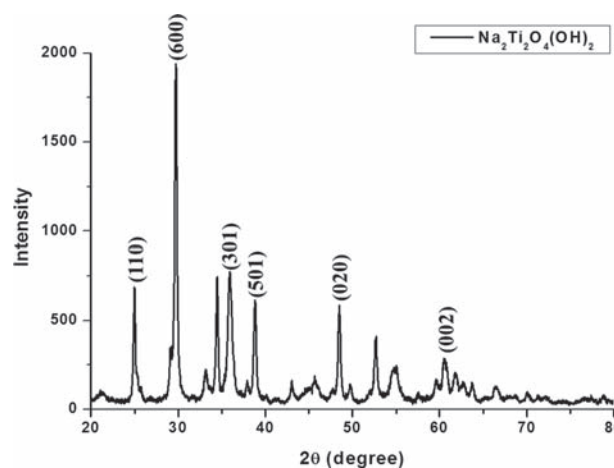


**Figure 1.** Low (A) and high (B) magnitude SEM images of sodium titanate nanobelts and top view (C) and cross-sectional view (D) of synthesized sodium titanate nanobelt electrode by doctor blade method.

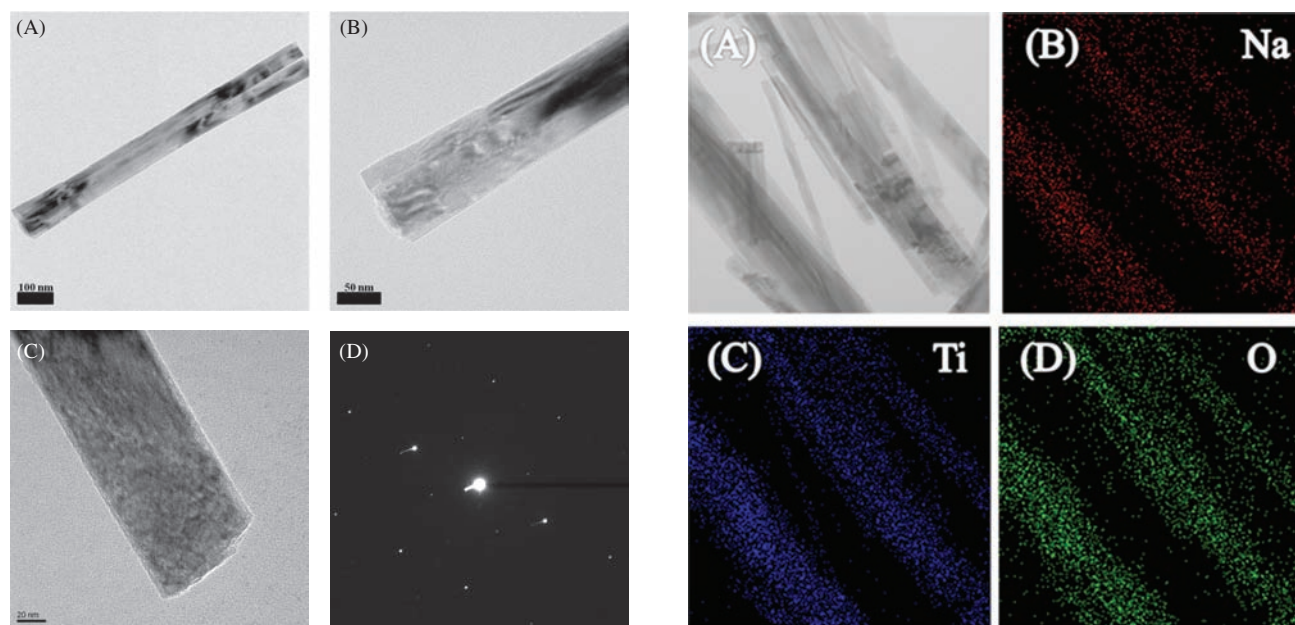
magnifications. A most of nanobelts with uniformed diameter around 100 nm. The length of the nanobelts was few tens of microns. Figures 1(C) and (D) are SEM image in top-view and cross-sectional view of sodium titanate nanobelt electrode fabricated by the doctor-blade method on the FTO glass surface. Fabricated sodium titanate photoanode has 8.5  $\mu\text{m}$  with appropriate thickness for fabrication of anode for DSSC.

XRD pattern of the sodium titanate nanobelts has shown in Figure 2. It really match with the standard JCPDS card No. 31-1329 of  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ .

Figures 3(A) and (B) shows the TEM image of the separated single nanobelt of the synthesized sodium titanate. It reveals that the belts are solid linear shape with 1.0–1.5  $\mu\text{m}$  in length and 70–80 nm in diameters. The selected-area electron diffraction (SAED) pattern has shown in Figure 3(D). It indicates that the nanobelts are single crystalline. To identify the crystal structure of the synthesized nanobelts, we examined the electron



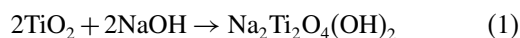
**Figure 2.** X-ray diffraction pattern of synthesized sodium titanate nanobelts.



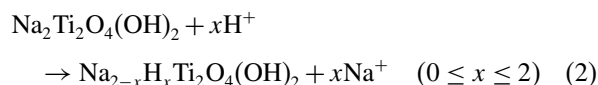
**Figure 3.** TEM images of sodium titanate nano belts has synthesized by hydrothermal process (A) and (B), HR-TEM image of sodium titanate nano-belts (C) and its SAED pattern (D).

diffraction patterns and the corresponding high-resolution electron micrographs in several orientations by tilting the nanobelts. The SAED pattern of  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  nanobelts lattice constants are:  $a_0 = 19.26 \text{ \AA}$ ,  $b_0 = 3.78 \text{ \AA}$  and  $c_0 = 3.00 \text{ \AA}$ . Since the layers of nanobelts of  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  are curved, the diffraction peaks related to the Z axis (e.g., 301, 501, 002) are much weaker than the peaks 200, 110, 600 and 020. To clarify electron composition of synthesized sodium titanate, EDS analysis with TEM has performed. Figure 4 shows the EDS elemental analysis and TEM image with matching EDS elemental mapping of sodium titanate nanobelts. Each element of sodium titanate was identified with EDS spectrum. The atomic weight percent of each elements are perfectly match with those of prepared  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ . The homogeneous compositions of Na, Ti, O elements were proved by EDS mapping images.

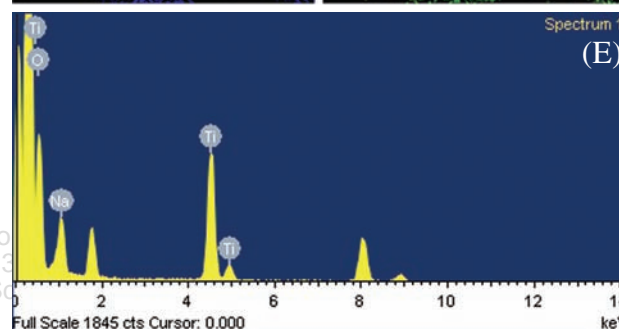
From the composition of nanobelts material stated above, the reaction formula of  $\text{TiO}_2$  (anatase) with concentrated NaOH can be written as follows (Eq. (1)):



In  $1 \leq \text{pH} \leq 13.5$  aqueous solution,  $\text{Na}^+$  can be exchanged with  $\text{H}^+$  (Eq. (2)):



Based on the above results and discussion, the material, which is has been previously denoted as “nanobelts  $\text{TiO}_2$ , nanobelts  $\text{TiO}_x$  or nanobelts  $\text{H}_2\text{Ti}_3\text{O}_7$ ,” is nanobelts



(F)

Element	Weight (%)	Atomic (%)
O K	36.86	58.16
Na K	15.01	16.48
Ti K	48.13	25.36
Totals	100.00	

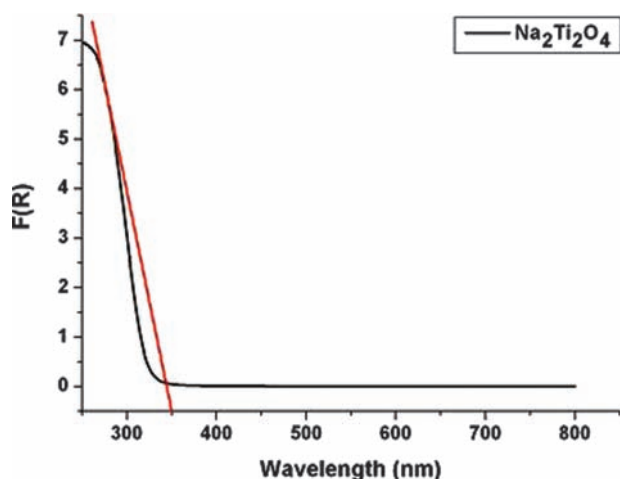
**Figure 4.** EDS element mapping images with TEM image (A), Na (B), Ti (C) and O (D). EDS spectrum for Sodium titanate (E), Table for each element weight and atomic ratio (F).

in  $\text{Na}_{2-x}\text{H}_x\text{Ti}_2\text{O}_4(\text{OH})_2$ , where  $x$  depends on the pH of the post-treatment solution.

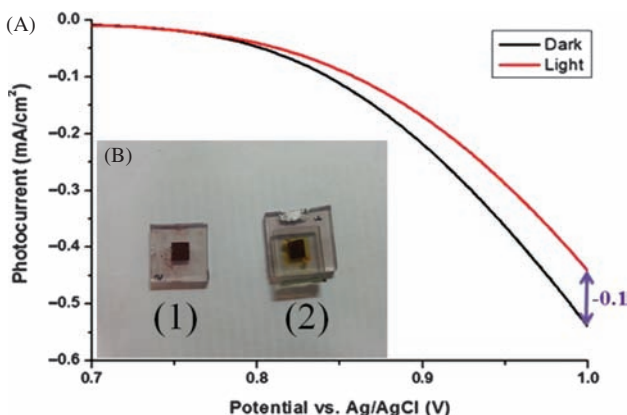
UV-Vis spectrum of sodium titanate nanobelts is shown in Figure 5. Tauc plot evaluating the optical band gap of sodium titanate is determined as 250 nm.

This is UV wavelength range and corresponding to 2.2 eV. The large band gap energy of sodium titanate nanobelts results in the low conductivity under the one sunlight. This causes so low photoconductivity of sodium titanate nanobelts under 1 sun light.

Efficiency of fabricated DSSC with fabricated sodium titanate nanobelts as an anode slightly increased in the light illumination (Fig. 6). It caused by the partial electron transport property of the sodium titanate rods by the



**Figure 5.** UV-Vis spectrum of sodium titanate nanobelts with Tauc plot.



**Figure 6.** Efficiency plot of fabricated sodium titanate nanobelt electrode under one sun light condition (red) and in the dark condition (black) (A). Images of dye absorbed photoanode (B-1) and whole DSSC cell (B-2).

excitation of the valence band electron to the conduction band energy level and photo-ejection to flow out to the anode electrode. It is already well known that the photoconductivity of the sodium titanate is intrinsically very low comparing with P25 Degussa  $\text{TiO}_2$  powder and the kinetics of the photo-decomposition of the organic 4-chloro-phenol showed less than twice of the P25 Degussa.<sup>10</sup> The further more work should be done to improve the photoconductivity of sodium titanate by doping with other transition elements.

#### 4. CONCLUSION

In summary, we have exploited a low-temperature solution-based method to large-scale synthesis of titanate

1D nanostructures. Sodium titanate nanobelts were synthesized successfully in gram quantities. We believe that this solution synthetic route, based on simple reactions with no participation of catalysts or templates, requiring no expensive equipment, and ensuring higher purity and uniformity of the products, will greatly reduce the production cost and offer great opportunity for large-scale synthesis of such 1D nanostructured materials. The morphology and crystal structure of prepared sodium titanate nanobelt has characterized by SEM, TEM, and XRD. The composition of the prepared sodium titanate nanobelts was characterized EDS and elemental mapping analysis. The band gap energy of prepared sodium titanate nanobelts has determined with optical absorption spectrum by Tauc plot evaluation. The photoconductivity of prepared DSSC with sodium titanate nanobelts as the photoanode were characterized by measuring the photocurrent versus to potential curves. Fabricated DSSC with sodium titanate showed good dye absorption property, but efficiency should be increased with further works.

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