

TiO₂ nanorods and semi-nanotubes prepared from anodic aluminum oxide template and their applications as photoelectrodes in dye-sensitized solar cells

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Anodic aluminum oxide (AAO) was used as a template coupled with liquid process for synthesis of TiO₂ nanorods and semi-nanotubes. Immersion setting (IS) and vacuum drop setting (VDS) were carried out to insert a TiO₂ precursor solution into AAO pores. With the calcination and NaOH aq. treatment to remove AAO, scanning electron microscopy (SEM) revealed that TiO₂ nanorods with diameter around 100–200 nm were successfully fabricated from IS, whereas TiO₂ semi-nanotubes were given from VDS. The synthesized nanorods or semi-nanotubes were mixed with commercial TiO₂ nanoparticles (P-25) with mixing ratios of 5:95, 10:90 and 15:85 (by mass). The optimum mixing ratios for nanorods and semi-nanotubes are 5:95 and 10:90, respectively. The photoelectrodes made with nanorods or semi-nanotubes showed better performances than the cells used of only P-25, because of the effects of one-dimensional (1-D) nanostructure.

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1. Introduction

Dye sensitized solar cells (DSSCs) have been expected to be candidates complementary to the silicon solar cells, due to their inexpensiveness and simplicity in manufacturing processes.^{1,2} The highest overall light-to-electricity conversion efficiency among the DSSCs was over 10%.¹⁻⁴ TiO₂ nanoparticles have been mostly used as photoelectrodes in DSSCs, due to the large surface area for dye adsorption and electron transportation pathway. However, the random contacts of TiO₂ nanoparticles at grain boundaries lead to trapping and recombination of electrons and holes, which limits the efficiency of the DSSCs.^{5,6}

Substantial efforts have been made to improve well-organized photoelectrode materials. These include ordered nanostructured materials, especially, one dimensional (1-D) structured materials.⁵ In these materials, greater photovoltaic performances may be gained through the development of the materials with improved electron transport.⁵⁻⁸ Ordered TiO₂ nanorods or nanowires are highly interesting candidates to reach this goal.^{5,6,8} There have been numerous methods to prepare TiO₂ nanostructures, including sol-gel process, electrospinning, and anodization of Ti metal.⁵⁻¹⁰ However, these methods have limitations in synthesizing highly ordered structures such as uniform TiO₂ nanorods or nanowires with accurately control of dimension and geometry. These factors strongly influence the diffusion of electrons, and consequently affect overall power conversion efficiency (PCE) of the DSSCs.^{5,11,12} Solution process with the use of

uniform templates is an alternative way to prepare uniform TiO₂ nanorods or nanowires with controllable dimension and geometry. K. Aisu et al.¹⁰ synthesized well-defined TiO₂ nanorods or nanowires using AAO-template method with the calcination and HCl treatment to remove AAO. Polycrystalline TiO₂ anatase nanorods and nanowires were successfully fabricated. The AAO template method became a very simple for the synthesis of TiO₂ nanostructures with uniformly ordered structure.^{9,11,12} By using hydrolysis reaction for insertion of precursor and changing a hole diameter and setting method of AAO or infiltration depth of precursor into AAO, size and aspect ratio of 1-D nanomaterials can be easily controlled.⁹⁻¹⁴

In our preliminary study, the nanorods with diameter of 100–200 nm were synthesized from AAO template and used in solar cells to slightly improve the efficiency.¹⁴ In that work,¹⁴ we used immersion setting (IS)¹⁰ to synthesize TiO₂ nanorods and applied in DSSC. The magnetic stirrer was used to mix a paste for photoelectrode of DSSC, which resulted in the agglomeration of nanostructures. Since many cracks on the surface were observed when coated only one time,¹⁴ the improvement of efficiency was limited.

In this study, AAO containing 100 and 200 nm pores were used as templates to prepare 1-D nanostructured TiO₂. The aim of this work is to control the diameter and shape of the nanostructured TiO₂, i.e. nanorods and semi-nanotubes, by pore diameter and setting method. An alternative method for removal of AAO template (i.e., using NaOH aq. treatment) was carried out. The obtained nanorods or semi-nanotubes were utilized as photoelectrodes in DSSCs. The sonication followed by magnetic stirring mixing was used for better dispersion. To reduce

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crack occurred on the surface, the photoanodes were coated for 2 times.

2. Experimental procedure

2.1 Fabrication and characterizations of TiO₂ nanorods

Ti[OCH(CH₃)₂]₄ (titanium tetraisopropoxide, TTIP) was used as a TiO₂ precursor and (CH₃)₂CHOH (isopropanol, i-PrOH) was used as a solvent. C₅H₈O₂ (acetylacetone, ACA) was used as a chelating agent.¹³⁾ ACA was added to slow down the hydrolysis reaction of TTIP. The composition ratio of TTIP:ACA was 1:1 (by molar) and the ratio of TTIP:(ACA+i-PrOH) was 1:4 (by volume).¹⁰⁾ The TiO₂ precursor solution was inserted into 1-D pore channels of AAO (Anodisc 13, Whatman) with pore diameters of 100 and 200 nm via immersion setting (IS) and vacuum drop setting (VDS) methods, respectively. After the insertion, the precursor was left in the air for 30 min to allow the hydrolysis reaction to occur (relative humidity of air was ~40%). Then, the samples were calcined at 450°C for 1 h in air. **Figure 1** shows a schematic illustration of the fabrication of TiO₂ nanorods and semi-nanotubes from AAO template.

2.2 Template dissolution

After calcinations, samples were immersed in 1 M hydrochloric acid aqueous solution (HCl aq.) for 72 h¹⁰⁾ or in 1 M sodium hydroxide aqueous solution (NaOH aq.) in a centrifuge tube for 1 h to remove AAO template from the samples. The samples were separated into solid phase (TiO₂ rich phase) and liquid phase by centrifuging at 10,000 rpm. Microstructure of AAO template, synthesized nanorods, synthesized semi-nanotubes, and commercial nanoparticles were characterized by a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi High-Tech, Japan, V_{acc} = 5.0 kV) and the chemical composition was analyzed by energy-dispersive X-ray spectroscopy (EDS). Crystal-line structures before and after NaOH aq. dissolution were investigated by an X-ray diffractometer (Multiflex, Cu-K α , 40 kV, 40 mA, Rigaku, Tokyo, Japan).

2.3 DSSC fabrication and characterizations

The obtained TiO₂ nanorods from IS and semi-nanotubes from VDS were mixed with pristine TiO₂ nanoparticles (AEROXIDE, P-25, Nippon Aerosil), and they were prepared as a paste for fabrication of a DSSC photoelectrode. The ratios of nanorods to nanoparticles and semi-nanotubes to nanoparticles in the mixing were 5:95, 10:90, and 15:85 (by mass). Each paste was coated directly on a conducting glass (indium-doped SnO₂ conducting glass, ITO, 10 Ω /sq.) by squeegee technique. The electrode was then calcined at 450°C for 1 h in the air. After the calcination, it was left to cool down to room temperature and then the prepared cells were immersed in an aqueous solution of titanium tetrachloride (TiCl₄, 80 mM). After that, the cell was calcined again at 450°C for 30 min. Next, the cell was immersed in 0.5 mM solu-

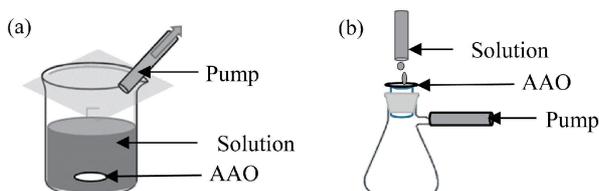


Fig. 1. Schematic illustration of (a) IS for synthesis of TiO₂ nanorods and (b) VDS for synthesis of semi-nanotubes from AAO template.¹⁰⁾

tion of ruthenium (II) dye (N719) in *tert*-butylpyridine and acetonitrile. The electrolyte used in this work was composed of dimethylpropyl imidazolium iodide, lithium iodide (LiI), iodide (I₂), and 4-*tert*-butylpyridine in acetonitrile.

The current density–voltage (J – V) curves were measured under simulated solar light (AM 1.5, 100 mW/cm²) using a solar simulator (XES-40S1, San-Ei Electric, Osaka, Japan). The light intensity of the illumination source was calibrated by using a standard silicon photodiode (BS520, Bunkoh-Keiki Co. Ltd., Tokyo, Japan). The photocurrent–voltage curves were measured by using a source meter (6241A, ADCMT, Tokyo, Japan). Dye absorption was estimated from the UV–Vis spectra (UV-3100 PC, SHIMADZU, Japan).

3. Results and discussion

3.1 XRD analysis for different template-dissolution processes

Figure 2 shows XRD patterns of the samples synthesized by AAO-template method using IS with/without template dissolution treatments. Without any treatment, weak peaks of anatase TiO₂ were observed with a broad peak of the amorphous AAO template. With 72 h HCl treatment, the broad peak of AAO disappeared, and the peaks of anatase were only observed. This result is in accordance to the previous report.¹⁰⁾ In order to reduce the time of the template dissolution step, NaOH aq. was used instead of HCl aq. The XRD pattern confirmed that only 1 h in NaOH, it was enough to dissolve AAO template, i.e. the peaks of anatase TiO₂ were only observed in the pattern. The XRD patterns of the samples synthesized by AAO-template method using VDS also showed the same results compared with these using IS (results not shown here).

3.2 Microstructure

For IS, when a commercial 100 nm-grade AAO template was immersed in TiO₂ precursor solution and dissolved in NaOH solution, the 1-D structured TiO₂ nanorods with a diameter of 100–200 nm and a length of 1–2 μ m were observed. The commercial AAO template used in this work is normally used as a liquid filter, so its pore diameters are not uniform through the 1-D pore channels.^{11),12)} The template has diameters at the top and the bottom of 100 and 200 nm, respectively, as shown in **Fig. 3(a)**. The thickness of a 100 nm-sized filter layer is only about 2 μ m on top of the template [**Fig. 3(b)**]. Therefore, varied diameters of nanorods between 100 and 200 nm were obtained from this method. Apart from TiO₂ nanorods obtained after dissolution, a formation of

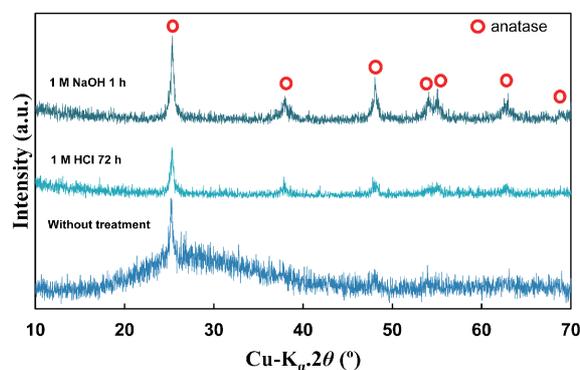


Fig. 2. XRD patterns of the samples from IS without treatment (including AAO template) and with treatments (to remove AAO template), using HCl treatment (1 M HCl at 40°C for 72 h) and NaOH treatment (1 M NaOH at room temperature for 1 h).

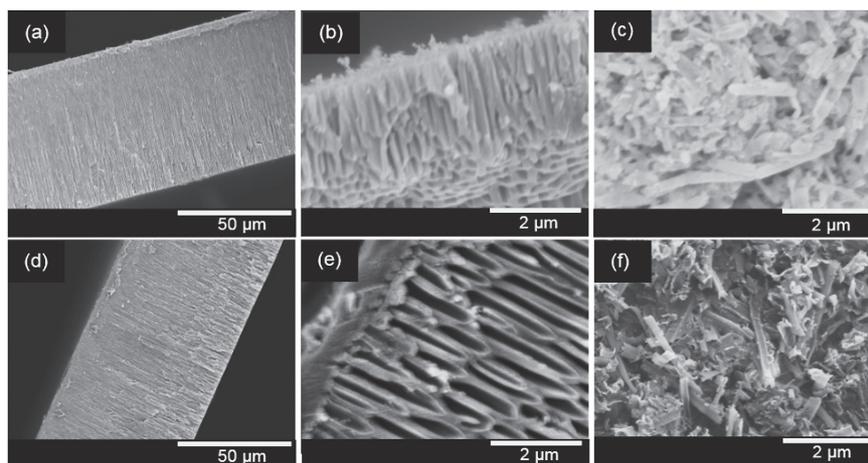


Fig. 3. SEM images of (a) vertical side of 100 nm-grade AAO template used in IS, (b) filter layer of 100 nm-grade AAO template, (c) synthesized nanorods via IS after AAO dissolution, (d) vertical side of 200 nm-grade AAO template used in VDS, (e) filter layer of 200 nm-grade AAO template, and (f) synthesized semi-nanotube structure via VDS after AAO dissolution.

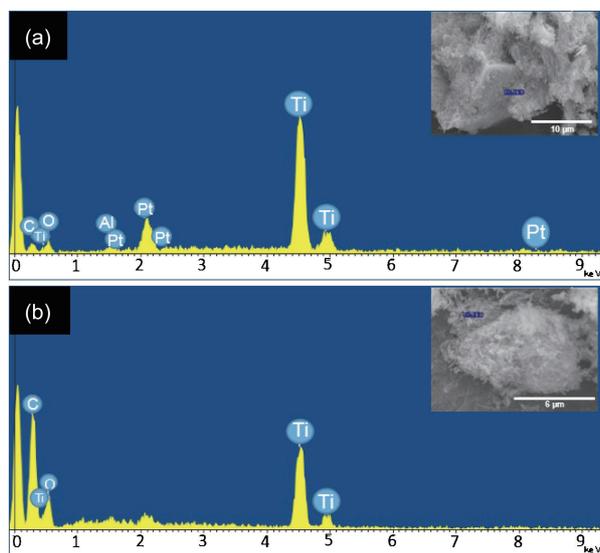


Fig. 4. EDS spectra of synthesized TiO₂ nanorods from IS at (a) wide and (b) specific areas. Insets indicate analysis positions from SEM images.

some TiO₂ nanoparticles was also revealed in Fig. 3(c).

For VDS, a commercial 200 nm-grade AAO template was utilized. Figures 3(d) and 3(e) show SEM images of the 200 nm-grade AAO template in different scales. The semi-nanotubes with length of 3–5 μm were observed after template dissolution [Fig. 3(f)]. These type of nanostructures might be obtained by the severity of the NaOH treatment with TiO₂ in AAO template induced transformation of nanotubes¹³⁾ instead of nanowires.¹⁰⁾ The result from VDS was different from IS, so it confirmed that diameter and length of nanostructured TiO₂ can be adjusted by changing the sample setting.^{7),10)–12)} Figure 4 shows EDS spectra of synthesized TiO₂ nanorods from IS. It was found that after dissolution in NaOH aq., only TiO₂ formed in nanomaterials in both wide and specific areas. These results confirmed again that amorphous Al₂O₃ from template was fully removed by NaOH treatment, which is a good agreement with XRD results.

3.3 TiO₂ paste for DSSC electrode

From XRD patterns in Fig. 5, the mixed paste from nanoparticles and 1-D nanostructures before and after calcination at 450°C from both IS [Fig. 5(a)] and VDS [Fig. 5(b)] consisted of mainly anatase¹⁶⁾ and small amount of rutile phase from P-25.¹⁷⁾ Figure 6 demonstrates the series of SEM observations. It can be deduced that a mixing process only by magnetic stirring resulted in nanostructure agglomerations. The particles and synthesized nanostructures were separated in the paste [Figs. 6(a) and 6(b)]. Coating for 1 layer using this paste lead to many cracks occurred on the surface [Fig. 6(c)]. Figures 7(a) and 7(b) show SEM images of pastes mixed by sonication followed by magnetic stirring. The dispersion of nanostructures were improved and cracks on the surface were somewhat reduced by the 2nd layer coating [Fig. 7(c)].

3.4 DSSC characterization

Figure 8 shows UV–Vis spectra indicating the absorption of dye on DSSC electrodes. For the 1 layer coating on the electrode, only NP had the highest dye absorption because of its larger surface area [Fig. 8(a)]. In contrast, the synthesized nanostructures mixed with nanoparticles (NR/NP or SNT/NP) even coated with 1 or 2 layers, dye absorption were decreased due to their smaller surface areas. Although the specific surface area of nanorods or semi-nanotubes are lower than nanoparticles, the photo-generated electron can move more efficiently along the 1-D structure to conducting glass because of the formation of bridged nanorods or semi-nanotubes in NP TiO₂ (as shown in Figs. 6 and 7). These structures reduce the possible loss of photoelectron and increase the performance of the cell. Table 1 shows the photovoltaic properties of DSSC for coated 1 layer electrode with various synthesized nanorod and semi-nanotube compositions. NP TiO₂ electrode was also given in the Table for comparison. The optimum nanorod content was obtained at 5 wt% in this study. The cell made from synthesized nanorods showed slight increase in *J*_{SC} can be contribute to improve in charge transport via electron express way concept.^{5),8),14)} The power conversion efficiencies (PCE) of cells were slightly improved, which are in good agreement with SEM observation about poor dispersion and agglomeration of nanorods [Figs. 6(a) and 6(b)] by only magnetic stirring. With improved mixing process and

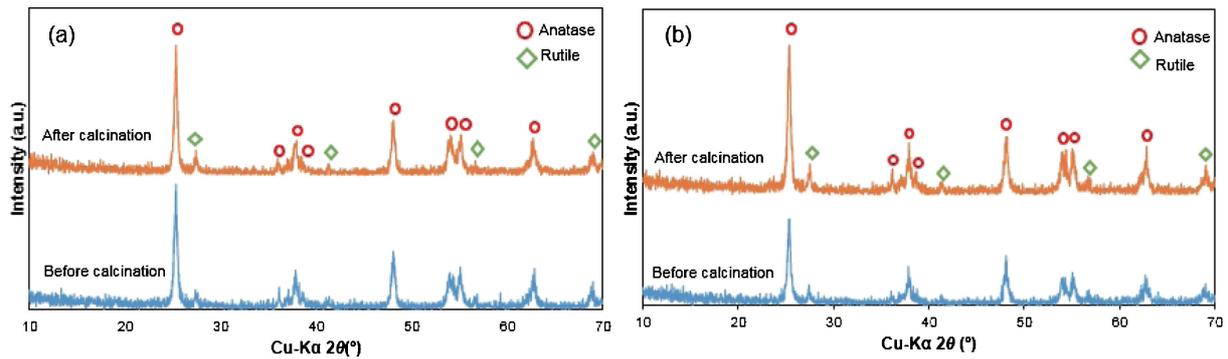


Fig. 5. XRD patterns of mixing paste between nanoparticles and nanostructures before and after calcination at 450°C fabricated from (a) IS and (b) VDS.

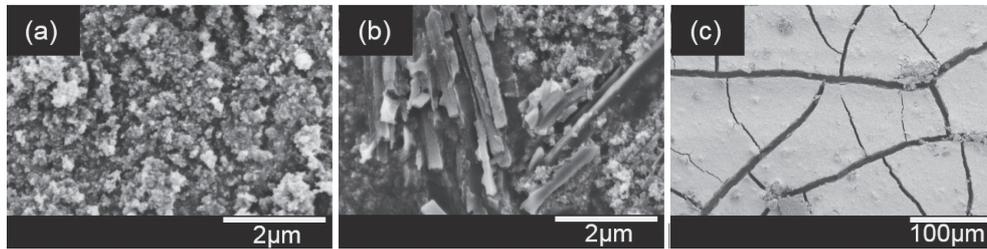


Fig. 6. SEM images of 1-layer coated TiO₂ paste of mixed nanorods (NR) from IS and nanoparticles (NP): (a) NP area, (b) agglomeration of NR, and (c) crack on electrode surface.

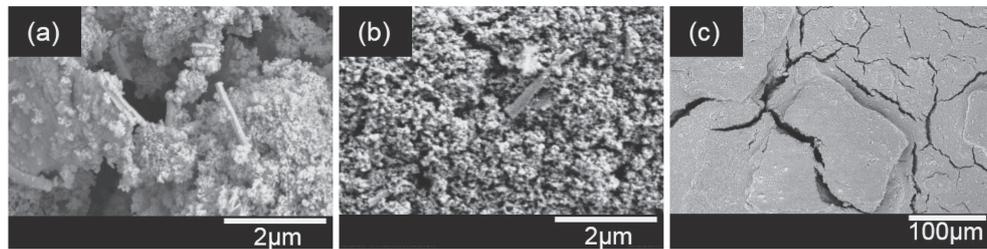


Fig. 7. SEM images of 2-layers coated TiO₂ paste of mixed semi-nanotubes (SNT) from VDS and nanoparticles (NP): (a) dispersion area at homogenous mixing, (b) no agglomeration of SNT, and (c) small crack on electrode surface.

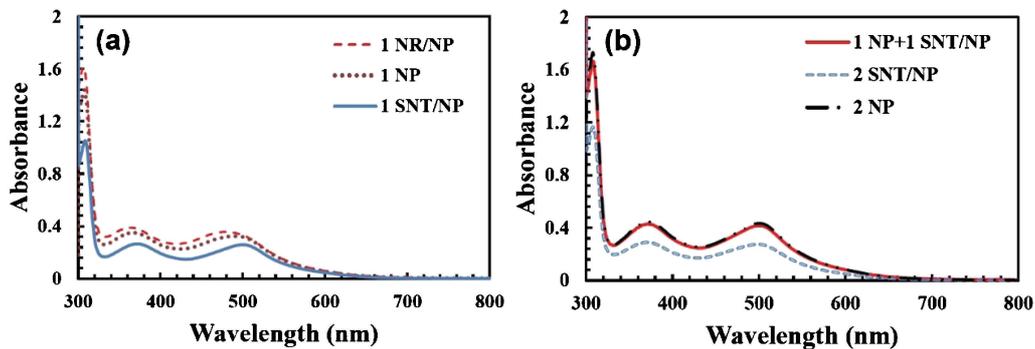


Fig. 8. UV-Vis spectra show dye absorption for comparisons of (a) coated 1 layer series from the best composition and a reference cell, and (b) coated 2 layer series from the best composition and a reference cell.

number of layers, the PCE was clearly improved from 4.11 to 4.77% as demonstrated in **Table 2**. Furthermore, the results can contribute to more advantages of synthesized nanostructures. The better dispersion of synthesized nanostructures and less crack on the surface improved charge transport, resulting more adhesion and bridging between nanoparticle and synthesized nanostruc-

tures.¹⁴⁾ The obtained optimum length of synthesized nanostructures did not exceed 10 μm, which help improved efficiency.¹⁵⁾

4. Conclusions

AAO containing 100 and 200 nm pores were used as a template for synthesis of TiO₂ nanorods and semi-nanotubes, respec-

Table 1. Cell performances of DSSC from nanoparticles (P25) and DSSC from nanorods (NR)/nanoparticles (NP) mixture (film thickness of ~20 μm)

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	Efficiency (%)
1 layer TiO ₂ NP	11.07	0.72	0.53	4.28
1 layer TiO ₂ NR/NP (5:95)	11.17	0.72	0.57	4.56
1 layer TiO ₂ NR/NP (10:90)	10.88	0.71	0.54	4.21
1 layer TiO ₂ NR/NP (15:85)	11.15	0.71	0.52	4.07

Table 2. Cell performances of DSSC from nanoparticles (P25) and DSSC from semi-nanotubes (SNT)/nanoparticles (NP) mixture (1 coating with film thickness of ~20 μm and 2 coating with film thickness ~30)

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	Efficiency (%)
1 layer TiO ₂ NP	11.07	0.72	0.53	4.28
1 layer TiO ₂ SNT/NP (5:95)	10.95	0.71	0.51	4.00
1 layer TiO ₂ SNT/NP (10:90)	11.27	0.74	0.56	4.68
1 layer TiO ₂ SNT/NP (15:85)	10.37	0.70	0.52	4.17
2 layer TiO ₂ NP	10.61	0.72	0.55	4.17
2 layer TiO ₂ SNT/NP (5:95)	11.72	0.70	0.51	4.20
2 layer TiO ₂ SNT/NP (10:90)	10.65	0.73	0.61	4.75
2 layer TiO ₂ SNT/NP (15:85)	9.61	0.73	0.52	3.82
2 layer TiO ₂ NP	10.61	0.72	0.55	4.17
1 layer TiO ₂ + 1 layer SNT/NP (5:95)	12.82	0.70	0.48	4.27
1 layer TiO ₂ + 1 layer SNT/NP (10:90)	11.92	0.70	0.57	4.77
1 layer TiO ₂ + 1 layer SNT/NP (15:85)	11.84	0.72	0.55	4.69

tively. Immersion setting (IS) and vacuum drop setting (VDS) were carried out to insert a TiO₂ precursor solution into AAO pores. With the calcination and NaOH aq. treatment to remove AAO, SEM characterization revealed that TiO₂ nanorods with diameter around 100–200 nm were successfully fabricated from IS, whereas TiO₂ semi-nanotubes with 200 nm pore diameter were successfully fabricated from VDS. The length of semi-nanotubes did not exceed 10 μm because of the shrinkage by heat treatment, NaOH aq. treatment, and magnetic stirring. The synthesized nanorods mixed with commercial TiO₂ nanoparticles (P-25) and the synthesized semi-nanotubes mixed with P-25 have optimum mixing ratios at 5:95 and 10:90 (by mass), respectively. The photoelectrodes made with nanorods or semi-nanotubes both showed better performances than the cells of only P-25. Due to the one-dimensional (1-D) nanostructure dispersion, the electron expressway concept was effective in this research.

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