Fabrication of electrospun BaTiO$_3$/chitosan/PVA nanofibers and application for dye-sensitized solar cells

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Abstract. Perovskite BaTiO$_3$ nanoparticles were synthesized by a hydrothermal method. BaTiO$_3$/chitosan (CS)/Polyvinyl alcohol (PVA) nanofibers with an average diameter of 265.3 $\pm$ 52 nm were fabricated via an electrospinning method. The nanofibers were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), and thermal analysis method (TGA). The photoanodes of dye-sensitized solar cells (DSSC) were fabricated based on the BaTiO$_3$/CS/PVA nanofibers. The photovoltaic properties of the cells were calculated based on the current density – voltage curves. The maximum power conversion efficiency of DSSC with CS/PVA/BaTiO$_3$ nanofibers was 0.49% with the natural dye sensitizer extracted from the leaf of the magenta plant.

Keywords: BaTiO$_3$ nanoparticles, BaTiO$_3$/chitosan/PVA nanofibers, dye-sensitized solar cells, electrospinning.

1. Introduction

The problem of energy in the new century is considered one of the issues of special concern. Renewable energy is one of the key technologies available to meet world energy needs. Solar power provides an abundant source of clean energy and will be a renewable energy source in the future. Thanks to DSSC’s simple design as well as its cost advantage, DSSC is a suitable choice. DSSC was invented by O’Regan and Gratzel in 1991 [1], and this is a photovoltaic device that works almost like natural photosynthesis. Scientists have tried to improve energy conversion efficiency through device configuration parameters, new substrate materials for commercialization, and long-term use of DSSC [2]. Indeed, most studies have shown that the problem of energy in the new century is considered one of the issues of particular concern focused on developing materials with a broader molar extinction coefficient. The other way is to increase photon conversion efficiency by increasing light absorption efficiency in the anode [3]. The approach possesses advantages such as cheap, easy-to-find materials, simple fabrication techniques, and easy improvement of many process stages, especially the application of nanotechnology to prepare materials with extensive surface areas [4].
The ferroelectric material BaTiO₃ has been studied for a long time with its high dielectric constant and distinct physical properties such as pyroelectric, piezoelectric, electro-optic, and nonlinear optic properties [5]. BaTiO₃ is used in applications related to energy conversion as DSSC. In conventional DSSC, the light was absorbed by a sensitized, attached to the surface of the type semiconductor with the most commonly used band gap is TiO₂. Still, some studies have shown that it could increase power conversion through perovskite materials such as CaTiO₃, BaTiO₃. BaTiO₃ is a type n semiconductor, which achieves a higher Vₜₜ than DSSC using TiO₂. There have been many studies on the application of BaTiO₃ as a semiconductor material in solar cells, such as Gireesh et al. [6], they demonstrated the ability of BaTiO₃ to be used as a photosensitive solar cell to replace TiO₂ with high efficiency BaTiO₃ has been synthesized by various techniques including the solid-phase reaction, sol-gel and hydrothermal method. Significantly, the hydrothermal method is critical as particle size, stoichiometry, and in some cases, particle shape can be controlled [7-9] on the apparatus configuration and the material system [10]. Electrospinning method uses electrical force to pull charged filaments of a polymer solution or molten polymer with fiber diameters on the order of a few hundred nanometers [11]. The technique has advantages such as low cost and ease of use, especially creating nano-sized polymer fibers. In recent years, researchers can be mentioned as Dissanayake et al. [12] using PAN nanofibers, Xu et al. [13] fabricating Bi-TiO₂ fibers. Moreover, the nanofibers obtained from this method can be doped with other substrates to evenly coat the sides of the anode and cathode for increasing the photovoltaic performance in this DSSC. This was proved by the study of Niel et al. on ZnO/TiO₂ nanofibers [14]. In addition, there are many studies on the preparation of BaTiO₃ through electrospinning by J Yuh et al. [15] with BaTiO₃/PVP fibers. In this study, DSSC was fabricated using BaTiO₃/CS/PVA nanofibers through electrospinning instead of traditional DSSC from TiO₂ material. Also, a counter electrode with GO synthesized [16] from coconut shell charcoal was studied to replace the current DSSC, which uses Pt substitution.

2. Materials and methods

2.1. Materials
The magenta plant was obtained at Xuan Khanh Market, Can Tho City, Vietnam. Polyvinyl alcohol (PVA), CS, sodium hydroxide (NaOH), acetic acid (CH₃COOH), formic acid (HCOOH), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), barium hydroxide octahydrate (Ba(OH)₂·8H₂O), and kali permanganate (KMnO₄) were purchased from Sigma. Potassium iodide (KI), iodine (I₂), titanium dioxide (TiO₂), ethanol (C₂H₅OH), hydroperoxide (H₂O₂), and ammonia solution (NH₄OH) were purchased from Xilong Inc. ITO glasses were provided by Welljoin Inc. Distilled water was used for all the experiments.

2.2. Methods

2.2.1. Synthesis of BaTiO₃ nanoparticles
BaTiO₃ particles were synthesized by a hydrothermal method [8]. Barium hydroxide octahydrate crystals was added to titanium dioxide powder with a ratio of Ba/Ti = 1.64 to obtain 10 mL of solution. 30 mL of ammonia solution (10 M) was added to the mixture and stirred for 15 min. The mixture was transferred to a 50 mL Teflon-lined stained-steel autoclave bottle. The hydrothermal reactions were carried out at 130 °C for 1 h. After the reaction, the container was cooled to ambient temperature. The resulting products were separated and washed with formic acid (0.1 M), ethanol, and water several times and dried in an oven at 60 °C for 24 h.

2.2.2. Preparation of BaTiO₃/CS/PVA nanofibers
CS was dissolved in 2 mL of acetic acid (3 vol.%) at room temperature for 3 h to obtain a CS solution (3 wt%). Then, PVA (11 wt%) was added into the CS solution under stirring at 80 °C for 5 h to obtain a CS/PVA solution. Next, BaTiO₃ nanoparticles (13 wt% based on solid materials) were added into the
CS/PVA solution and stirred for 1 h to form a BaTiO$_3$/CS/PVA solution. The BaTiO$_3$/CS/PVA solutions were electrospun with the fixed conditions: applied voltage of 15 kV, tip-to-collector distance of 15 cm, and feeding rate of the solution of 0.5 mL/h.

2.2.3. Fabrication of DSSCs

Preparation of natural dye sensitizers:
Magenta leaves were dried at 50 °C to saturated moisture content (about 3.3 wt%) and crushed into fine powder. The natural dye was extracted by soaking 2 g of the fine powder into 12 mL of ethanol (50 wt%) and HCl (1 wt%) at 40 °C for 6 h. The extracted solid was filtered to obtain a dye solution [17].

Preparation of working electrode and counter electrode
The working electrode was prepared with three types of DSSCs, including BaTiO$_3$ films, BaTiO$_3$/CS/PVA films, BaTiO$_3$/CS/PVA nanofibers. ITO glass substrates with an effective area of 1 cm $\times$ 1 cm were washed with ethanol and dried. BaTiO$_3$ film and BaTiO$_3$/CS/PVA film on cleaned ITO glass substrates were prepared using a doctor blade technique and sintered at 200 °C for 20 min. BaTiO$_3$/CS/PVA nanofibers were deposited on ITO glass substrates using an electrospinning process conducted at proper conditions for 10 min. The working electrodes were treated by a thermal method at 200 °C for 20 min to remove the residue solvents and were then soaked in the dye solution for 12 h at room temperature. GO was prepared from coconut shell charcoal by Hummer’s Modified method [16]. GO sheets were used as a catalyst at the counter electrode.

DSSC assembling
The electrolyte was prepared by mixing 0.83 g of potassium iodide and 0.127 g of iodine with 10 mL of ethylene glycol under stirring at 300 rpm for 30 min [18]. Three kinds of DSSCs were prepared based on BaTiO$_3$ films, BaTiO$_3$/CS/PVA films and BaTiO$_3$/CS/PVA nanofibers. DSSC was fabricated by sandwiching the working electrode and counter cathode, and the electrolyte was injected into the middle of the electrodes by a micro syringe. The J-V curves were determined from the photoelectric measurement of the devices with an active area of 1 cm$^2$.

2.2.4. Characterizations
Scanning electron microscope (SEM, Hitachi, S4800, an accelerating voltage of 10 kV after gold coating) was used to observe morphologies of electrospun BaTiO$_3$/CS/PVA nanofibers. X-ray diffraction (XRD) was applied to characterize the crystal structure of the BaTiO$_3$ and electrospun BaTiO$_3$/CS/PVA nanofibers by using a D8 Advance Brucker at 2 theta in the range of 10° - 80°. The absorption spectrum of BaTiO$_3$ nanoparticles was measured on a UV–Vis spectrophotometer (UV-Vis, Pharo 300, Merck) at room temperature. TGA analysis was carried out on a TGA instrument (NETZSCH) with a calibrated platinum pan in the temperature range from 30 to 800 °C at 20 ºC/min. Fourier-transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Scientific) was applied to characterize the functional groups of BaTiO$_3$ and BaTiO$_3$/CS/PVA nanofibers.

3. Results and discussion

3.1. Characteristics of materials

3.1.1. UV-Vis results and the band gap energy of BaTiO$_3$ nanoparticles
Figure 1 shows the UV-Vis spectrum and Tauc plot of the BaTiO$_3$ nanoparticles. The UV-Vis spectrum results were calculated using the Tauc plot method in order to determine the band gap energy (E$_g$) of the BaTiO$_3$ nanoparticles [19,20].

\[(\alpha h \nu)^2 = K(h \nu - E_g)\]
where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, $K$ is the energy-independent constant. The value of $h\nu$ is 1240 as obtained from the Planck equation. The value of $\alpha$ is 2.303 as calculated from the absorbance data using the Beer-Lambert’s Law. The absorbance coefficient is calculated by the equation based on the absorbance ($A$) and the cuvette path length ($L=1\text{ cm}$)

$$
\alpha = \frac{A \times L}{0.4343}
$$

The absorption edges of the BaTiO$_3$ are 386 nm and 397 nm, respectively. Thus, the band gap energy of BaTiO$_3$ nanoparticles was estimated by the Tauc plot to be 3.03 eV.

![Figure 1. UV-Visible spectrum and band gap energy of BaTiO$_3$ nanoparticles](image1)

3.1.2. SEM results of BaTiO$_3$/CS/PVA nanofibers

![Figure 2. SEM image and diameter distribution of electrospun BaTiO$_3$/CS/PVA nanofibers](image2)
Figure 2 shows an SEM image of BaTiO$_3$/CS/PVA nanofibers and the distribution of nanofiber diameters. The suitable conditions for electrospinning were 11 wt% of PVA solution, CS/PVA weight ratio of 8/2, 5 wt% of BaTiO$_3$ based on solid materials, 15 cm of tip-to-collector distance, and 0.5 mL/h of feeding rate. Electrospun BaTiO$_3$/CS/PVA nanofibers were uniform. The diameters of electrospun nanofibers were from 100 nm to 500 nm. By randomly choosing 100 fibers and using ImageJ software, the fiber average size was 265.3 nm with a standard deviation of 52 nm.

3.1.3. X-ray diffraction results

![XRD pattern](image)

Figure 3. XRD patterns of a) PVA, b) CS, c) BaTiO$_3$ nanoparticles, d) electrospun BaTiO$_3$/CS/PVA nanofibers

Figure 3 illustrates the XRD patterns of materials. The diffraction peaks at the 2θ of 21.8°, 25.12°, 31.22°, 38.53°, 44.8°, 50.54°, 55.84°, 65.52°, 70°, 74.45°, 78.65° corresponding to the lattice planes (100), (101), (111), (200), (201), (211), (202), (103), (230) and (311) could be exactly assigned to BaTiO$_3$ phase. According to Scherrer's equation, the average crystallite size of BaTiO$_3$ was 40.107 nm. This result is completely consistent with the previous study [21]. Compared to pure CS and PVA, the peak at 2θ of 19.7° is the characteristic peak of PVA and CS [22]. Thus, BaTiO$_3$/CS/PVA nanofibers were successfully fabricated by the electrospinning method.

3.1.4. FTIR results

Figure 4 shows the FTIR spectra of CS, PVA, BaTiO$_3$ and BaTiO$_3$/CS/PVA. The peak at 643 cm$^{-1}$ is assigned to Ti–O stretching vibration. The broad peaks at around 1253 cm$^{-1}$ indicates Ba–Ti–O stretching vibration. The peaks at 1655 cm$^{-1}$ and 750 cm$^{-1}$ indicate the presence of the amine group (N-H) of CS. The peak at 1728 cm$^{-1}$ represents the C=O bond of the carboxylic group. The broad and strong peak at 3360 cm$^{-1}$ is assigned to the OH stretching vibration of CS and PVA. The sharp peak at 2915 cm$^{-1}$ indicates the asymmetric stretching of the -CH$_2$ groups (Figure 4b). The sharp peak at 2900
cm\(^{-1}\) of BaTiO\(_3\) indicates the remaining formic acid (Figure 4a). In addition, there is no chemical bond formation among CS, PVA, and BaTiO\(_3\).

Figure 4. FTIR spectra of a) BaTiO\(_3\) nanoparticles, b) BaTiO\(_3\)/CS/PVA nanofibers

3.1.5. The results of thermal gravimetric analysis of BaTiO\(_3\)/CS/PVA nanofibers

Figure 5 shows the TGA curve of electrospun BaTiO\(_3\)/CS/PVA nanofibers. An increase in the temperature increased from 30 °C to 250 °C, the weight loss of the nanofibers was 13.6% due to water and acetic acid remaining in the electrospun nanofibers. The derivative thermogravimetric (DTG) curve shows two endothermic peaks at 95 and 185 °C. The major mass loss took place in the second
step from 250 °C to 530 °C. The weight loss of nanofibers was 72% due to the phase change of the polymers, polymer structure degradation, and the carbon combustion, relating to the three weight-loss peaks at 323 °C, 443 °C, and 505 °C in the DTG curve. The second decomposition stage shows the maximum decomposition rate around 323 °C with the highest weight loss. Finally, the percentage of the remaining material was approximately 13% of BaTiO$_3$ based on the dry materials.

3.2. Photovoltaic study
The performance of DSSCs with BaTiO$_3$/CS/PVA nanofibers is determined by density – voltage (J-V) measurement given in Figure 6. The solar energy-to-electrical energy conversion efficiency ($\eta$) DSSCs can be defined as the ratio of electrical power to the optical power incident on a DSSC. $\eta$ can be expressed as follows [23]:

$$\eta = \frac{I_{SC} \cdot V_{OC} \cdot FF}{P_{in}}$$

where: $I_{SC}$ is short-circuit current, $V_{OC}$ is open-circuit voltage, FF is fill factor, and $P_{in}$ is incident optical power.

![Figure 6. The J-V plots of DSSCs using BaTiO$_3$ films, BaTiO$_3$/CS/PVA films, and BaTiO$_3$/CS/PVA nanofibers, with the dye of the leaf of magenta plant.](image)

| Working electrode       | $I_{SC}$ (mA) | $V_{OC}$ (V) | FF   | $\eta$ |
|-------------------------|---------------|--------------|------|--------|
| BaTiO$_3$/CS/PVA nanofibers | 1.79          | 0.40         | 0.67 | 0.49   |
| BaTiO$_3$/CS/PVA films    | 1.42          | 0.38         | 0.65 | 0.36   |
| BaTiO$_3$ films           | 1.23          | 0.39         | 0.56 | 0.27   |
The photoelectrochemical parameters of the DSSCs were shown in Table 1. The solar cell prepared by electrosprun BaTiO$_3$/CS/PVA nanofibers had the open-circuit voltage of 0.413 mV, short-circuit current of 1.8 mA, and fill factor of 0.67. The solar energy-to-electrical energy conversion efficiency of the cell with BaTiO$_3$/CS/PVA nanofibers was 0.49, which is higher than that of BaTiO$_3$/CS/PVA films or BaTiO$_3$ films as working electrodes. It can be explained that the fibrous film can transmit light more efficiently than the dense films. Besides, the addition of CS in the doping system and the use of the natural ingredient, namely anthocyanin photoreceptors from the magenta plant helps to deal with environmental issues and cost. CS is composed of β-(1,4) 2-amino-deoxy-D-glucopyranose bonds in which the presence of nitrogen and oxygen make it suitable as a host for polymer electrolytes.

4. Conclusion
Perovskite BaTiO$_3$ nanoparticles with a band gap of 3.03 eV were synthesized by a hydrothermal method. The electrosprun BaTiO$_3$/CS/PVA nanofibers with an average diameter of 265.3 ± 52 nm were successfully prepared. The content of BaTiO$_3$ in electrosprun nanofibers was about 13%. The working electrodes of DSSCs were designed based on the BaTiO$_3$ films, BaTiO$_3$/CS/PVA films, and the BaTiO$_3$/CS/PVA nanofibers. A maximum solar energy-to-electrical energy conversion efficiency of 0.49% was obtained for the BaTiO$_3$/CS/PVA nanofibers as a working electrode with the natural dye sensitizer extracted from the leaf of the magenta plant.

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Conflict of interest
The authors declare that there is no conflict of interest.

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