

Facile and mild preparation of brookite TiO₂ nanoparticles with small sizes

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Research Article

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Abstract

In this study, we used hydrothermal treatment with different metal cation as additive to prepare small size brookite TiO₂ with large surface area. The obtained brookite nanoparticles is provided with both high crystal phase purity and smaller uniform particle size (~10 nm). The small size brookite TiO₂ as photoanode material of DSSCs retains the advantages of higher open-circuit voltage, and improvement of higher short-circuit current density by larger specific surface areas. It has best photoelectric conversion efficiency reached 6.48%, which is comparable to commercial P25. This research therefore provides a facile and mild synthetic method of small size brookite nanoparticles as excellent photoanode materials.

1. Introduction

Among all the transition-metal oxide materials, titanium dioxide (TiO₂) is the most widely used semiconductor material. Environmental friendliness, cost-effectiveness and excellent photochemical properties is the main attraction of TiO₂[1]. Anatase, rutile and brookite are the three representative polymorphs of TiO₂. Among them, almost all of paper focus on the research of rutile and anatase. Anatase has the significantly high photocatalytic activity while rutile is the most stable phase of all [2]. By contrast, strict synthesis condition for obtaining phase pure brookite lead to brookite remains one of the least studied crystalline of TiO₂ [3].

Generally speaking, metastable phases demonstrate better behavior in photoelectrochemistry than the stable counterparts [4]. Hence, brookite as a kind of having a relatively lower symmetry and higher surface energy metastable TiO₂ polymorphs can further enhanced photoelectrochemistry properties [5]. It is well known that photoelectric conversion efficiency can be affected by the open-circuit voltage (V_{OC}) in DSSCs. Brookite with most negative conduction band (CB) potential is to the benefit of conversion efficiency on the premise of three TiO₂ crystal phases have similar valence band (VB) [6]. Moreover, the appropriate depth of electron traps of brookite is also one of the advantages relative to anatase or rutile [7, 8].

Except for the difficulty in preparing brookite with high phase purity, another hurdle is how to obtain large surface area brookite nanoparticles. Some report proved the photoelectronchemistry activity of nanocrystalline is related to crystalline structure, crystallite dimension, morphology features, specific surface area [9, 10]. Therefore, facile and mild synthetic routes should be researched to prepare brookite nanostructures with controllable feature and size. The small size brookite with large surface area can add active sites to improve photoelectrochemistry potential of brookite-based DSSCs to a considerable extent.

In this paper, brookite TiO₂ nanoparticles with large surface area can be obtained by an easily synthetic method. Used different metal cation as additive in hydrothermal treatment can prepare small size brookite TiO₂ nanoparticles successfully. The reduction of particle size can lead to larger surface area, resulting higher dye-loading content and photocurrent in DSSCs. The solar conversion efficiency of larger surface area brookite-based DSSC could reach 6.48%, which is comparable to commercial P25. The facile

and mild preparation of brookite TiO₂ nanoparticles with small sizes is conducive to its practical application.

2. Experimental

All the Brookite TiO₂ nanoparticles products were prepared through hydrolysis of TiCl₄ via a one-pot hydrothermal reaction. Initially, clear and transparent solution can be obtained by TiCl₄ was added drop-wise into 40 mL iced deionized water. After precursors preparation, 5.0 g urea were added into the above solution to adjust pH value, while 5.0 mL of sodium lactate liquor (60%) was used as complexing agent. Stirring until completely dissolved, 1 mol% Bi(NO₃)₃·Sr(NO₃)₂·Pb(NO₃)₂ solution was added into the solution and keep stirring, respectively. The uniform resulting mixture transferred into a 100 mL autoclave that was allowed to react at 200°C for 20 h. The precipitate of TiO₂ were collected by centrifugation and washed with water and absolute ethanol to attain neutral pH value. And finally, the product was allowed to dry at 70°C in air overnight and then calcined at 500°C for 3h.

The photoelectrode can be obtained by blade coating TiO₂ paste on fluorine doped tin oxide (FTO) glass. Later, coated glasses were sintering in the muffle furnace and immersed in N719 (Solaronix) ethanol solution (0.3 mM) dye for 20h in the dark. The DSSC devices were fabricated with sensitized photoanode and Pt counter electrode in a sandwich type structure.

3. Results And Discussion

3.1. Crystal phase and morphology analyses

The XRD patterns of products prepared with different metal cation were characterized and shown in Fig. 1. The peaks of products with Bi³⁺·Sr²⁺·Pb²⁺ ions have no difference with the products without metal cation as additive. Indexed in accordance with JCPDS 65-2448, all the diffraction peaks are consistent with orthorhombic brookite phase. No diffraction peaks of anatase or rutile phase can be observed in Fig. 1. It shows that the addition of three kinds of metal cation did not change the crystalline phases, which remain the pure brookite phase TiO₂.

It's worth noting that the diffraction peaks mentioned above obviously broaden relative to the synthesis without metal cation. Scherrer equation deduced theoretically the relation between grain size and degree of diffraction line width, $D = \lambda / \beta \cos \theta$. It shows the smaller size of the product, the wider diffraction peaks. The broadened diffraction peaks in Fig. 1 show the addition of Bi³⁺, Sr²⁺ and Pb²⁺ ions result in smaller size brookite nanoparticles successfully. It is generally known that the reduction of particle size can increase the surface area of brookite nanoparticles, thereby show better performance in DSSC. The ionic radius of Ti⁴⁺ ions is 0.605 Å while the ionic radius of Bi³⁺, Sr²⁺ and Pb²⁺ ions is 1.03 Å, 1.18 Å and 1.19 Å, respectively. The ionic radius of metal cation is much larger than Ti⁴⁺ ions. During the process of crystal nucleation and growth, termination of crystal growth will take place when the heterogeneous

atoms bring in inerratic arrange crystal. Hence, the metal cation as additive can inhibiting crystal growth and then obtain smaller size brookite nanoparticles. Moreover, according to the previous research on synthesis metastable phase brookite, Na^+ or Ca^{2+} ions usually used as a stabilizer when hydrothermal reaction. It's worth noting that the ionic radius of Na^+ (0.97 Å) or Ca^{2+} (0.99 Å) ions are similar to the ionic radius of Bi^{3+} , Sr^{2+} and Pb^{2+} ions, which larger than that of Ti^{4+} (0.605 Å). Thus the Bi^{3+} , Sr^{2+} and Pb^{2+} ions with similar ionic radii relate to Ca^{2+} and Na^+ ions can also act as stabilizers. In conclusion, smaller nanoparticles and high purity brookite TiO_2 can be obtained by introduction of Bi^{3+} , Sr^{2+} and Pb^{2+} ions.

Moreover, there is no shift of the diffraction peak indicate metal cation did not doped in crystal. Generally speaking, the difference of the ionic radius should be less than 20% so that the heterogeneous ionic can be doped in crystal. The ionic radius of metal cation above are almost two times larger than Ti^{4+} ions, so it is hard to be doped. The diffraction peaks of at $2\theta = 30.8^\circ$ become slightly weaker, this is due to crystallinity of present product be not a patch on brookite without metal cation. From the above, the addition of metal cation can result in smaller size brookite nanoparticles, which is benefited to be used in DSSC.

The crystallite dimension and morphologies of the brookite TiO_2 synthesized with different metal cation can be observed in Fig. 2 FESEM micrographs. As can be seen in Fig. 2a, brookite without metal cation (denoted as BTN) have a uniform pseudo-cube morphology, which size is about 50 nm. All the brookite products with metal cation exhibit much smaller sizes than BTN particles, which is consistent with the result of XRD patterns. The brookite adding Bi^{3+} ions (denoted as BTB) displayed regular aggregated nanoparticles, the average particle size was found to be 10 nm. At the same time, the brookite adding Sr^{2+} (Fig. 2c, denoted as BTS) or Pb^{2+} ions (Fig. 2d, denoted as BTP) are a mixture of nanoparticles and a small quantity of nanorods. The size of spherical particles is about 10 nm and the rods have a length of 100 nm.

3.2. Photovoltaic performance analyses of the solar cell

All the brookite nanoparticles with different metal cation used as photoanode to fabricate DSSCs, the current density-voltage ($J-V$) graphs are presented in Fig. 3a. The corresponding photovoltaic parameters of the DSSCs can be obtained according to the $J-V$ graphs and given in Table 1.

As compared to anatase solar cells, the V_{OC} of all brookite solar cells tends to increase. This can be explained with the help of higher Fermi level of brookite TiO_2 than anatase TiO_2 . Not only that, but charge recombination can also be decreased effectively on account of the lower reactivity of the brookite surface. It should be noted that BTB, BTS and BTP based solar cells show slightly lower V_{OC} values than the BTN one. On one hand, there is typical function relation between band gap and grain diameter according to the transformed Kubelka-Munk equation. The band gap presented a positive correlation to the grain diameter from 29 to 17 nm, which because of quantum size effect and delocalization of molecular orbitals. On the other hand, comparing with the BTN particles, smaller particle size of BTB, BTS

and BTP result in more boundaries. The boundaries cause more surface trapping and electron recombination phenomenon. To sum up, it can be concluded that lower band gap value and more surface boundaries influence on the lower V_{OC} of the BTB, BTS and BTP based solar cells.

Nevertheless, as shown in Table 1, the BTB, BTS and BTP film-based solar cells give superior efficiency than BTN film-based one even though the lower V_{OC} . The photovoltaic conversion efficiency (η) of BTB, BTS, BTP and BTN film-based solar cells is 6.12%, 6.48%, 6.46% and 3.22%, respectively. All the small size brookite solar cells show excellent photovoltaic performance comparable to anatase solar cells. The key reason is the much higher J_{SC} . The J_{SC} of BTB, BTS and BTP film-based solar cells is almost twice as large as BTN. The much smaller particle sizes of BTB, BTS and BTP particles result in larger specific surface areas as compared to the BTN. Larger specific surface areas can provide more adsorption sites to increase dye loading, increasing the absorption of visible light. In addition, a small quantity of nanorod brookite with ~ 100 nm long diameter in BTS and BTP can have a synergistic effect. The nanorod brookite with larger size can be used as a scattering material to enhance light harvesting, improving the J_{SC} value of the solar cell.

3.3. Photoelectrochemical behavior analyses of the solar cells

The electrochemical impedance spectra (EIS) can further study of the electronic and ionic processes during the DSSCs operations. Figure 3b shows their Nyquist plots of DSSCs fabricated from different brookite photoanode. The impedances of R_s of BTB, BTS and BTP were 19.09, 18.07 and 18.20 Ω , respectively. All the R_s with smaller size brookite are lower than that of BTNs (31.83 Ω). The smaller particle sizes of brookite make for reduced contact resistance. As shown in Table 1, the electron transfer resistance (R_2) of BTB, BTS and BTP is almost half of BTN. This can be ascribed to the increased charge transfer capacity. The smaller particles size brookite can adsorb more dye molecule and show better electron injection efficiency, resulting an in overall photovoltaic performance boost.

4. Conclusion

In the present study, we successfully synthesized high purity brookite TiO_2 nanoparticles by a facile and mild hydrothermal method. The grain size was decrease with different metal cation as additive. The metal cation can inhibit crystal growth and then obtain smaller size brookite nanoparticles. The larger specific surface areas can provide more adsorption sites to increase dye loading, thereby improving the J_{SC} . The pure brookite-based DSSCs not only preserve the properties of higher V_{OC} , but also overcome the drawbacks of lower density anchoring sites on the brookite surface. The solar conversion efficiency of larger surface area brookite-based DSSC could reach 6.48%, improving the availability of brookite TiO_2 nanoparticles in DSSCs.

Declarations

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Data Availability

The data used to support the findings of this study are all included within this article.

Conflict of interest The authors have not disclosed any competing interests.

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Table

Table 1 Photovoltaic properties of DSSCs.

Device	$J_{sc}/\text{mA cm}^2$	V_{oc}/V	FF	$\eta/\%$	R_s/Ω	R_1/Ω	R_2/Ω
BTN	6.48	0.71	0.70	3.22	31.83	2.44	53.51
BTB	12.18	0.69	0.73	6.12	19.09	2.54	27.76
BTS	13.93	0.69	0.67	6.48	18.07	2.69	25.81
BTP	13.14	0.69	0.71	6.46	18.20	2.63	26.61

Figures

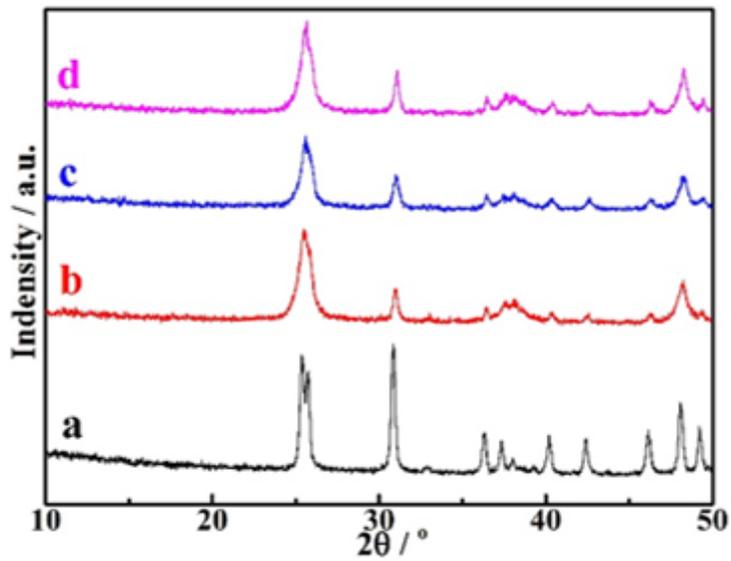


Figure 1

XRD patterns of the obtained BTN (a), BTB (b), BTS (c) and BTP (d) particles.

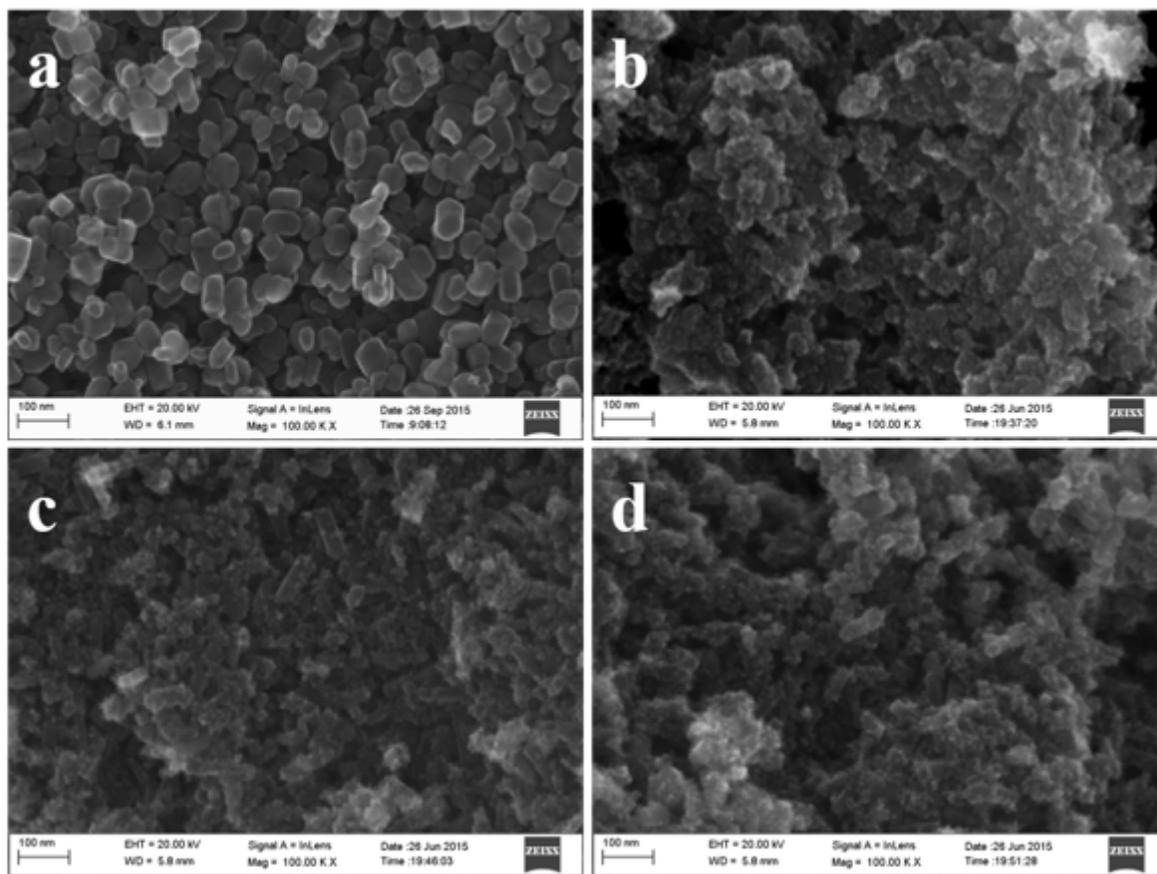


Figure 2

FESEM images of the obtained BTN (a), BTB (b), BTS (c) and BTP (d) particles.

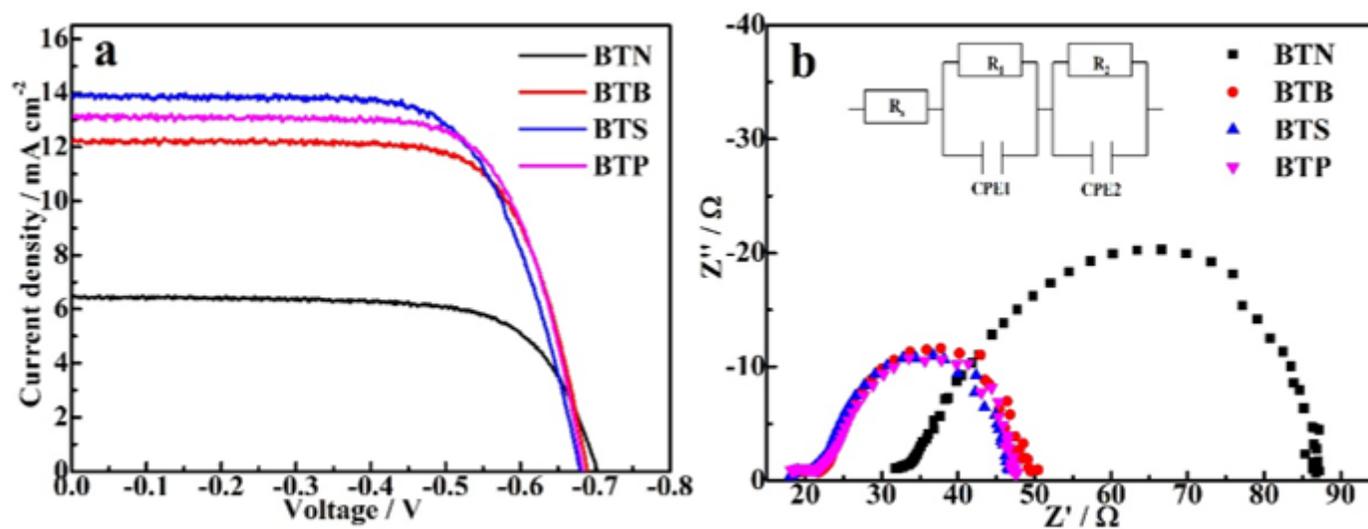


Figure 3

Comparison of J - V (a) and EIS (b) curves of the DSSCs fabricated with the BTN, BTB, BTS or BTP film.