The Formation and Particle Management of ZnTiO$_3$ to Meet the Demand of UV Protection of Perovskite Solar Cells

Xiang-yu SUN, Jing WEI, Qian WANG and Ming LEI

Corresponding author

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Abstract. The instability under UV light has always been one of those pivotal obstructions hindering perovskite solar cells (PSCs) from industrialization. In this work we introduced a convenient way which not only enhance the accuracy of calibration but also successfully reduce the size of ZnTiO$_3$ nanoparticles to effectively match with the device in protecting the light harvesting layer from UV decomposition.

Introduction

For a very long period of time, since discovered in 2013, the work around perovskite solar cell (PSC) was mainly about improving its photoelectric conversion efficiency. Contribute to the effort of research staff all over the world, the efficiency of PSCs has been dramatically improved from 2% [1] to 23.2% [2]. Though PSC is now qualified to compare with the first-generation silicon-based solar cell in efficiency aspects, there’s still some obstructions hindering it from industrialization, such as high toxic of lead component in light harvesting layer; low tolerance of moisture; relatively low endurance of heat[3] and can be decomposed by exposure to ultra-violet light[4,5]. In this work we focus on providing a convenient way to protect the absorption layer from UV decomposition without separately adding an additional shelter outside the device.

Research and Discussion

Aiming to maximize both the ability of UV harvesting and device stability and minimize the influence to the transmission of light in other bands, we start to filter the possible candidate. ZnTiO$_3$, contribute to its perovskite structure, which means it can match the perovskite harvest layer properly with less dislocation, and its poor photocatalysis, was chosen to form a dense layer to protect the device.

ZnTiO$_3$ (ZTO) is a semiconductor with relative wide bandgap, so in conventional methods it’s hard to obtain a high purity product with uniformed particle in relatively low temperature such as high temperature solid phase method[6] which requires a temperature more than 1000°C with unsatisfied product quality; High energy ball milling mechanical activated solid phase method[7] which relatively reduced the time scale of processing but the purity of the product was poor; molten salt method[8] which uses relatively low melting point salt to reduce the temperature and enhance its purity, but it’s large particle scale (1~3um) is too big to feat with the device, etc. Sol-gel method is a method to use precursor form a sol-gel mid-product fist and then obtain the wanted oxide through heat treatment. Contribute to its molecule/particle level mixture and its mechanical milling free process the product can be uniformed in particle size with high purity.

Firstly we tried to form such a layer through a sol-gel process directly on the indium doped tin oxide (ITO) glass which came out that the layer we formed was too thick to match our demand and caused by the high temperature calcination step it’s almost impossible to form an additional layer without changing the device structure. After that referencing the successful preparation and film formation of low-temperature TiO$_2$ nanoparticle, we decided to prepare the ZTO nanoparticle through a low temperature (600°C) sol-gel process[9] first and then disperse it in 2-methoxy ethanol with PEG surfactant to form a ZTO ink which significantly simplify the whole process of device manufacture[3].Comparing the two TiO$_2$-based PSCs and ZTO-based PSCs, the latter achieved a
reliable 19.8% efficiency and the best of them had remained 90% of its peak efficiency even experienced 100h of UV exposure (365nm, 8mW cm⁻²) while the former had dramatically decayed to 80% of its initial efficiency in 5h[10]. This paper mainly focused on analyzing the synthesis process and provide an easy-access way to obtain a high qualified optimized size ZTO particle.

Figure 1. The SEM image of ZTO(left) and the TEM image of ZTO(right).

The whole synthesis started with preparing the TiOSO₄ precursor. First of all, metatitanic acid was used to produce TiOSO₄ precursor. Before the TiOSO₄ was filtered to get the transparent solvent, it was cooled down to room temperature, doubled the dilution and added in activated carbon to absorb the impurity caused by the impurity of the industrial metatitanic acid we use. Traditionally the calibration Ti⁴⁺ concentration in the TiOSO₄ solution takes at least three or even more times of repeating work which has poor efficiency and low accuracy. Here we recommend a more convenient way to obtain a more accurate result. The pre-order operation was the same with the traditional method and we get the light purple solvent (for more details see the preparation section). The solvent was then added into six transparent test tubes 4mL each and added 400uL ammonium thiocyanate into these tubes as indicator. Take one tube as rough test, use ammonium ferric sulfate as titrant instilling while oscillating until the solvent turns into reddish steadily and doesn’t vanish with oscillation. Take this amount of ammonium ferric sulfate as a scale bar, and use the other 5 tube as a density spectrum (varies 20uL~40uL of ammonium ferric sulfate between each depending the accuracy required) and observe through the bottom of the tube to maximize the color difference among each tube. Find the one nearest to turn into reddish and repeat this density test once to both improve both the accuracy and liability of the calibration. Then we mixed TiOSO₄ with ZnSO₄ with a Ti/Zn ratio if 1/1 to form the ZTO precursor sol. Na₂CO₃ was used to adjust the pH of the solution into 7 in the sol forming process:

\[ TiOSO_4 + (n + 1)ZnSO_4 + (n + 1)H_2O + (n + 2)Na_2CO_3 \rightarrow \]

\[ ZnCO_3 \cdot nZn(OH)_2 \downarrow + TiO(OH)_2 \downarrow + (n + 2)Na_2SO_4 + (n + 1)CO_2 \uparrow \]  \hspace{1cm} (1)

Originally uncertain amount of PEG400 was added as a surfactant to prevent the particle from agglomeration, and the particle they obtain was roughly around 60~130nm[9]. Through previous experience of forming thin film through dispersed nanoparticles, this size of particle is hard to form a uniform dense film with no holes between the ITO and the light sensitive layer. By controlling the adding speed of Na₂CO₃ solution and the adjust the amount of PEG400 in the solvent to enhance its performance, without the support of a new additive or raising the sintering temperature, we successfully control the main size of the ZTO nanoparticle from 60~130nm to 10~20nm (Figure 2). Here the adding speed of Na₂CO₃ mainly influences the texture of ZTO precursor. When it was added rapidly, after drying and grinding the precursor was crispy and was in a more sand-like form.
On the contrary a gently added production was apparently denser while milling. These differences was mainly caused by the CO$_2$ produced during the sol forming process (1). When Na$_2$CO$_3$ was added rapidly the gas was produced in a high speed preventing the precursor to form a continuous uniform gel product and suppressed these separate gels to form porous agglomerates. After drying these agglomerates provides the foregoing sand like texture and in some aspects inducted the gel to form large scale agglomerates. So, by slowing down the adding speed, assisted by adjusting the surfactant PEG400 into a proper amount, a unified gel can be formed and weaken the possibility of agglomeration during heating process(2).

$$\text{TiO(OH)$_2$ + ZnCO$_3$\cdot nZn(OH)$_2$} \rightarrow \text{ZnTiO$_3$+H}_2\text{O↑+CO}_2 \downarrow$$ (2)

Compare to the original size, a smaller particle size can form a more dense and thinner layer which plays an important role for an additional layer to maximize its protection of UV while minimize its affection to the processing of the whole device. The device based on ZTO has successfully reached a high efficiency of 18% with 1.11Voc and 73%FF compare with it the device based on TiO$_2$ shows only 16% efficiency, 1.06Voc and 65.5%FF. (Figure 2).

![Figure 2. Photovoltaic J–V curves performance of ZTO and TiO$_2$ based devices.](image)

The Preparation of ZnTiO$_3$ and Device

The Preparation of TiOSO$_4$

Add 18mL sulfuric acid slowly into the mixture of 12g Metatitanic acid and 9mL ultrapure water. Then stir at 75℃ for 4~5h. After cooling down, add 27mL ultrapure water and 5g activated carbon and stir for another 12h in room temperature. Filter the mixture to obtain the transparent TiOSO$_4$ solvent.

Certify the Concentration of Ti4+in the TiOSO$_4$ Solvent

Use saturated sodium bicarbonate solvent to liquid seal the 500mL Erlenmeyer flask after add 500uL TiOSO$_4$ solvent with 24.5mL ultrapure water, 25mL (36%) hydrochloric acid and 2g Aluminum foil into it. Heat for 15~20min to let the reaction complete. The the solvent in the flask should be light purple. Add 4mL solvent into six transparent test tubes and then added 400uL ammonium thiocyanate into these tubes as indicator. Take one tube as rough test, use ammonium ferric sulfate as titrant. Instilling while oscillating until the solvent turns into reddish steadily and doesn’t vanish with oscillation. Take this amount of ammonium ferric sulfate as a scale bar, use the other 5 tube as a density spectrum (varies 20uL~40uL of ammonium ferric sulfate between each depending the accuracy required) and observe through the bottom of the tube to maximize the color.
difference among each tube. Find the one nearest to turn into reddish and repeat this density test once to both improve both the accuracy and liability of the calibration.

**The Preparation of ZnTiO$_3$**

Mix ZnSO$_4$ solvent with TiOSO$_4$ solvent in the proportion of Zn:Ti=1:1(mol) using moderate amount (solvent volum:PEG400 volume=6:1) of PEG400 as Surfactant. Add saturated Na$_2$CO$_3$ into the solvent gently until the pH = 7. The solvent was stirred during the whole process. The precipitation was washed with ultrapure water 5~6 times until the SO$_4^{2-}$ was completely washed off (use BaCl$_2$ as a indicator), than dried at 80°C and grinded before calcined at 600°C for 3h.

**The Preparation of Device**

The glass/ITO substrate was cleaned by sonication in deionized water, acetone, and isopropanol. Dissolve 18 mg ZTO powder and 5 mg PEG8000 into 2 mL 2-methoxy ethanol to prepare the ZTO ink. Spin coat the ZTO ink on glass/ITO substrates in ambient air before annealed at 150 °C for 30 min to obtain the ZTO electron transport layer. The TiO$_2$ layer was spin-coated on glass/ITO substrates from the colloidal TiO$_2$ nanocrystal solutions, and then annealed at 150 °C for 30 min. The colloidal TiO$_2$ nanocrystal solutions was made following the report from Hairen et al.[10] The perovskite film was prepared following procedures reported in ref. [11]. The hole-transport layer (HTL) was subsequently deposited on the perovskite film by spin coating at 4000 rpm for 30 s. The HTL precursor was prepared by dissolving 72.3 mg Spiro-OMeTAD, 29 µL mL$^{-1}$ tert-butylpyridine, 18.5 µL of bis(trifluoromethane) sulfonimide lithium salt (520 mg mL$^{-1}$ in acetonitrile), and 28.5 µL FK209 (300 mg mL$^{-1}$ in acetonitrile) into 1 mL chlorobenzene and stirring 30 min at normal temperature. After that, 55 nm of gold were deposited evaporation at ≈10$^{-6}$ Torr as an electrode.

**Summary**

By optimizing the certify process of the concentration of Ti$^{4+}$ in the TiOSO$_4$ solvent, we can obtain a more reliable and accurate result in a convenient method and contributed to the adjustment to reduce and unify the ZTO nanoparticle size, forming a dense and thin film has become possible. Based on all these works, we finally further accomplished the process of adding a ZnTiO$_3$ thin UV absorbing layer to significantly enhance the endurance to UV light without reducing the efficiency of the device.

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**References**


