

Research article

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Study On Influence of Lead-Free Sensitizer With Various Zno Based Photoanode Structures

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ABSTRACT

This paper provides the information about the systematic background of the Lead-free sensitized solar cell. A model of lead-free perovskite sensitized solar cell is designed with the effective, eco friendly sensitizer CH₃NH₃SnCl₃.calculating their efficiencies and studying the interaction of the sensitizer with different combinations of photoanodes are discussed, such as pure ZnO, Nb₂O₅ core-shell structure with ZnO, Al₂O₃ doped ZnO and Nb₂O₅ doped ZnO are serving as an ETM layer of perovskite sensitized solar cells of PSSC 1, PSSC 2, PSSC 3 and PSSC 4 respectively. The optimum parameters are measured and the efficiency of all four structures 87%,85%,60% and 33% have been achieved for PSSC 3, PSSC 4, PSSC 2 and PSSC 1 respectively. From the simulation, an efficient lead –free sensitizer play a remarkable role in the perovskite sensitized solar cell and is confirmed by J-V characteristics and EIS studies are discussed.

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1 INTRODUCTION

In recent years, organometal halide perovskite solar cells (PSSCs)have attracted the significant interest of research community due to their optoelectronic behavior, high power conversion efficiency(PCE)and low manufacturing cost. Organolead halide perovskite material is applied for producing perovskite solar cells. Great progress has been realized in the device fabrication and significant improvement of device performance has been achieved, as shown by the recently reported efficiency of 19.3%, in comparison with 3.81%, the efficiency of the first perovskite solar cell reported in 2009.^{1,2}. The PCE of CH₃NH₃PbX₃ PSSC has reached approximately 22% in2016.³. However, such kind of material lacks long-term stability, toxic and brings a severe health issue. The toxicity of typical perovskite solar cell can be avoided by using CH₃NH₃SnCl₃ which has a direct band gap of the value 1.30ev as a surface absorbing layer. It has the most appropriate optical properties and the light absorption range among all the CH₃NH₃BX₃(B=Sn, X=Cl, Br, I)compounds for an optoelectrical application. Recent studies have revealed that ZnO Can be used as a Proper substitute of Tio₂ as the ETM layer without affecting the performance of PSSCs significantly^{4,5}. It has a direct band gap of 3.37ev. such a wide band gap leads to high electron transport mobility.

The efficiency of such solar cell can be effectively modified by proper suitable doping material and sensitizer. In our present work, the doping agent with ETM material, such as Al and Nb₂O₅ can alter the bandgap of ZnO. The band gap size or width is increased by the addition. Which leads to fast electron mobility and high electron density (η). Charge transport and resistivity studies of hybrid halide perovskites have largely focussed on their semiconducting (electron/hole transport) behavior, and indicate high carrier mobility and long minority-carrier diffusion lengths⁶⁻⁹. Current-voltage characteristics show a hysteresis in photovoltaic performance¹⁰⁻¹⁴. Spectroscopic impedance studies suggest that the hybrid perovskites might exhibit ionic charge transport in addition to electronic conduction.

A model of a lead - free perovskite sensitized solar cell is proposed. Device simulation has been done for Glass/FTO/ZnO/ $CH_3NH_3SnCl_3$ /HTM/Carbon. For a ZnO can be modified by ZnO with Al, ZnO with core-shell of Nb₂O₅ and ZnO doped with Nb₂O₅ are used as photoanode of the PSSCs.We have considered Spiro-OMe TAD as the HTM layer for all type of simulation. The interaction and influence of $CH_3NH_3SnCl_3$ with these photoanode structures are discussed and the results are tabulated.

2 EXPERIMENTAL PROCEDURE

2.1 PREPARATION OF ZINC OXIDE NANO PARTICLE

4 mol/L NH₃·H₂O solution was slowly dropped into the 0.5 mol/L Zn(NO₃)₂ solution with a speed of 3 mL/min which was first added into a 250 ml three-necked flask, and the mixed solution was gently stirred, and the reaction temperature was controlled at 60 °C. The addition of NH₃·H₂O was stopped when the pH of the mixture reached pH 8.0. The mixture was stirred continuously for 30 min. The suspension was aged for 5 h at 60 °C, and then was filtered. The sample was washed with deionized water and ethanol for several times to make sure that the residual impurities were removed. The product was atmospherically dried at 80 °C for 5 h and then calcined at 500 °C for 1 h in a muffle furnace with a heating rate of 5 °C/min. The final product was a white powder¹⁵.

2.2 PREPARATION OF ZnO-Nb₂O₅CORE/SHELL NANO PARTICLE

The Nb₂O₅ precursor solution was prepared from 0.02 M NbCl₅ solution in anhydrous ethanol. The solution was dropped on to the ZNPs layer and spin-coated to remove the residual precursor solution. The Nb₂O₅ coating thickness was modulated by the number of coatings applied. Finally, the substrate was sintered at 500 °C for 30 min to complete the conversion into a crystallized Nb₂O₅ layer ¹⁶.

2.3 PREPARATION OF Al₂O₃ DOPED ZnO PARTICLES

A solution of zinc acetate (2 mmol) and $AlCl_3$ (2 mmol) in EtOH/H2O solvent (30 mL) was added to a solution of NaOH (6 mmol) at room temperature under stirring. After 30 min stirring the mixture transferred into Teflon-lined stainless steel autoclaves, sealed and maintained at 150 °C for 24 h. Subsequently, the reaction was cooled down to room temperature immediately. The resulting white solid products were centrifuged, washed with distilled water and ethanol to remove the ions, possibly remaining in the final products, and finally dried at 60 °C in the air ¹⁷.

2.4 FABRICATION OF PSSCs

The prepared photoanodes of pure ZnO nanoparticles, ZNPs/ Nb₂O₅ core/shell and Al@ZNPs paste coated in the thickness of 10 μ m by doctor blade technique on FTO glass plate (8–10 Ω /square) of an active area of 1cm2. CH₃NH₃SnCl₃ layer was sensitized by a repeated sequential deposition method. Firstly 1M SnCl₂ was dissolved in N, N-dimethylformamide (DMF) and spin coated onto the photoanode film at a speed of 2000 RPM for 60s and then heated at 100 °C for 5 min to remove DMF solvent. After it was cooled to room temperature, then the film was spin coated again to get a relatively thick and smooth film, which were subsequently heated at 100 °C for 30 min. SnCl2 films were kept in 10 mg/mL CH₃NH₃Cl isopropanol solution for 10 min, then rinsed with isopropanol to give CH₃NH₃SnCl₃ absorber layer of thickness 400 nm. Finally, the photoanode/ CH₃NH₃SnCl₃ film

was heated at 100 °C for 30 min in the air with a hot plate. The perovskite sensitized photoanode was coated with Ta_2O_5 blocking layer by dipping precursor solution, followed by sintering at 450 °C for 20 min. The thickness of Ta_2O_5 blocking layer was controlled by dipping time and was measured by 15 nm. Four types of PSSCs were fabricated using the CH₃NH₃SnCl₃ perovskite sensitized photoanode namely pure ZnO without blocking layer (PSSC-1), ZnO/ Nb₂O₅ core/shell structure without blocking layer (PSSC-2), Al₂O₃/ZnO with blocking layer of Ta₂O₅ (PSSC-3), ZnO/ Nb₂O₅ core-shell structure with blocking layer of Ta₂O₅ (PSSC-4). Spiro-OMeTAD is used as a hole transporting materials (HTM) for all photoanodes sandwiched together with graphite coated counter electrode. A graphite coated counter electrode was then clipped on top of the photoanode to form a photovoltaic device.

2.5 CHARACTERIZATION OF PSSCs

The PSSCs were characterized by recording the photocurrent-voltage (J–V) curves under illumination of A.M. 1.5 G (100 mW/cm2). The photoanode samples were characterized by X-ray diffraction (XRD) on X'Pert PRO-PANalytical X-ray diffractometer. Morphology of the samples was recorded by transmission electron microscope (TEM) PHILIPS TECNAI10 model operated at 200 kV. The surface morphology and composition of elements presented in the photoanode sample was examined by scanning electron microscope with energy dispersive X-ray spectrometer (SEM/EDX) VEGA3SB model. Electron impedance spectra of PSSCs were recorded with potentiostat/galvanostat (Gamry-300). The applied bias voltage and AC amplitude were set at an open-circuit voltage of the PSSCs and 10 mV between the working electrode and the counter electrode. The frequency range explored was 1 MHz to 105 Hz. The impedance spectra were analyzed by an equivalent circuit model, interpreting the characteristics of the PSSCs through Zsimpwin software.

3 RESULT AND DISCUSSION

The X-ray diffraction pattern confirmed to the structure of the pure ZnO nanoparticle, /ZnO and Nb2O5 core-shell/ZnO structure.From the Figure it could be absorbed that the sharp diffraction peak of pure ZNPs at (1 0 0), (0 0 2), (1 01), (1 0 2), (1 0 3), (2 0 0), (1 1 2), (2 0 1) and (2 0 2). All the diffraction peaks are well crystallized and indexed to the hexagonal ZnO wurtzite structure (JCPDS no. 36-1451). The peaks at 35.15° , 43.35° , 52.50° and 57.50° are indexed to the Al phase and the peaks at 34.37° , 36.19° , 43.82° , 47.49° , 56.54° , 62.80° corresponds to the planes respectively.(8 0 0), (8 2 0), (7 7 0), (0 0 2), (12 4 0), (8 4 2) of Nb2O5phase (JCPDS card No. 72-1484)¹⁸. From the XRD results, the diffraction peaks confirming the high purity of the synthesized products.

The microstructural analysis provides the information about all the four types of PSSCs. The image illustrates ZnO nanoparticles are spherical in shape with a smooth surface and the size of the particles around 20–50 nm and the size of the nanoparticles is less than 50 nm which is in good agreement with the particle size calculated from the Debye–Scherrer formula of XRD pattern. Al₂O₃ /ZnO also exhibits spherical in size with the diameter varying between 10 and 30 nm. This implies that the particle is smaller in size as compared to the pure ZnO. The results are in good agreement with the XRD pattern. The core-shell Nb₂O₅/ZnO exhibits the spherical in nature with the smooth surface ¹⁹. The morphology of the photoanode samples is found to be very uniform, quite clean, and smooth-surfaced.

3.1 PERFORMANCE COMPARISON OF PSSC_s BY DIFFERENT ZnO BASED PHOTOANODE MATERIAL WITH THE SENSITIZER

To evaluate the effectiveness and usability of our proposed lead-free ZnO based PSSCs, needs a verification accompanied by J-V curve, EIS study. Methylammonium tin chloride perovskites are thought to be a potential substitute to conventional methylammonium lead chloride perovskite because it has a direct bandgap of1.3ev.Besides, it is earth abundant and free of toxicity. For Nb₂O₅ core-shell/ZnO with CH₃NH₃SnCl₃, Nb₂O₅ doped ZnO with CH₃NH₃SnCl₃ and Al-doped ZnO with CH₃NH₃SnCl₃ structure, the efficiency is 3.81,7.60 and 9.41 while the fill factor is 65%,69% and73% respectively. From the table, we can see that the overall performance of all structures. The efficiency and fill factor has shown a good improvement in Al-doped ZnO based PSSC. The open circuit voltage and short circuit current have also shown a significant change in PSSC-3. Thus the results justify the possibility of the successful combination of Al-doping with the ZnO PSSC model.

The choosing of Electron-transport layer (ETL), such as ZnO is a good adapting material for doping in Photo-Voltaic devices. The influences of the sensitizer CH₃NH₃SnCl₃ with the additive material of photoanode are determining the efficiency function of the cell.Niobium(v)pentoxide was selected as an additive for ZnO in PSSC-2. When Niobium with 5 valance electron is introduced to Zn with 4 valence electrons, excess electrons are introduced in the 3d band and can play the role of the donor. The addition of Nb into the ZnO layer of the perovskite CH₃NH₃SnCl₃ structure showing high PCE in PSSC-2 and PSSC-4, the efficiency of both cells is increased as compared to PSSC-1. Which indicates the suppression of light reflection would increase the conversion efficiencies of the cell.

Two mechanisms could be considered to explain the decrease of the sheet resistance of ZnO. The first one is Nb doping at the Zn sites in the ZnO structure. From XRD, we noted that the ZnO phase still preserved the crystal structure, energy gap, the transparency of ZnO. In addition, a small amount of Nb is widely distributed in the ZnO phase, as can be confirmed by SEM. The excess electrons of Nb could be introduced into the 3d band of Zn and act as a donor. Another possible mechanism is carrier transport enhancement by the formation of Nb-rich particles in the ZnO layer, as observed by SEM. Nanoparticles in the electron transport and hole transport layer could enhance the carrier transport ^{20,21} and Nb-rich particles might also contribute to carrier transport. Both mechanisms would result in an increase in carrier concentration and in the improvement of photoconversion efficiency through the increase in JSC.

The efficiency of a perovskite solar cell depends largely on the response of solar spectrum.which is influenced by the sensitizer of the ETM layer. It plays a vital role in the overall performance of the solar cell. The sensitizing layer used in the photoanode will absorb more photons, which in turn will create more electron-hole pair; the chances of recombination are reduced and the electrons are easily diffused by this way.

Figure (1) represents a photocurrentdensity-voltage (J-V) characteristics of devices constructed with the $CH_3NH_3SnCl_3$ perovskites as light harvesters. The photovoltaic parameters are summarized in the table(1). It is found that the short circuit current (JSC) and efficiency of solar cell increases in the order of PSSC (3)> PSSC (4) > PSSC (2) > PSSC (1) due to greater influences of the sensitizer $CH_3NH_3SnCl_3$ with these ETM materials.since the perovskite material has a direct band gap1.3ev and also have a high absorption coefficient.

A small amount of sensitizer can lead to a high power conversion efficiency (PCE). It is found in the PSSC-3. Which implies that the PSSC 3 have a successful combination of the material of photoanode Al /ZnO/ CH₃NH₃SnCl₃, it yields a high PCE as compared all other PSSCs.

From all these cases, we found there is a rule on it.compare with pure ZnO, all the dopant material that could raise the conversion efficiency due to their matched energy level with the photoanode material, whose conduction band is higher than ZnO and their valance band is lower than ZnO. Here ZnO/Al₂O₃ has a longer energy gap and matched energy level position. Once irradiated, the electrons from sensitizer can transport through the potential barrier to the conduction band of ZnO by electron tunneling effect. The potential barrier generated by Al₂O₃ can effectively forbid the electron for recombination, so the dark current is hampered. Life and carrier concentration of Al₂O₃ doped photoanode is increased by the layer of Al₂O₃. Cl atom present in the sensitizer could lengthen the diffusion length of excitons²². The perovskite CH₃NH₃SnCl₃ sensitizer solar cell of PSSC-3 shows higher photoconversion efficiencies. In the study present here, the energy gap of the Al-ZnO/ CH₃NH₃SnCl₃ /Spiro-OMeTAD structure is increased through the influence of Cl atom present in the Sensitizer, Which could contribute to the increase of open circuit voltage. The PCE of PSSC

2,3,4 are increased, but PSSC-3 has a higher efficiency in the group. Which indicates PSSC-3 is good for adopting the Cl atom compare to all other PSSCs, it leads to a higher conversion efficiency.

EIS technology is a common electrochemical technique to determine the current bias in PSSCs.It can be used to explore effectively impedance characteristics of the electron transfer process²³. The Nyquist diagram was shown in figure (2). In the EIS, three arcs represent three different kinds of impedance. In the high-frequency region, the arc represents the impedance of interface between the carbon electrode and electrolyte; in the middle-frequency region, the arc represents the impedance among sensitized ZnO/ electrolyte interface; in the Low-frequency region, the arc represents the diffusion resistance inside the electrolyte.

It can be seen from the figure(2)that with the Al_2O_3 doping PSSC-3 indicates, the radius of the Arc in the middle-frequency region increased gradually. The larger the radius, the lager the impedance is. This reveals that the sensitizing layer of Al_2O_3 decreased the transmission resistance of electron among the group. This, in turn, decreased the recombination rate of an electron, which reduced the dark current and promoted the electron transfer towards the external circuit. We conclude that the Arc radius of Nb_2O_5 core-shell and Nb_2O_5 doping structure of ZnO photoanode(PSSC2 and PSSC4) in the middle region is increased as compared with pure ZnO but it has decreased when compared to PSSC3 due to the energy level of Nb_2O_5 is not well matched with that energy level of ZnO. Therefore, the conversion efficiency of the cell is reduced.

In the case of PSSC3, it is well recognized that Rtr is one of the major factor influencing the FF of the solar cell. This arises mainly from three factors: the active and interfacial layer resistance, electrode resistance and contact resistance. We estimated Rtr and Conc value of PSSC-3 decreases as compared to PSSC1,2,4. This results show,not only the decreased rate of recombination but also enhanced the ncc of PSSC-3. The recombination rate is inversely proportional to the recombination resistance. The increase of electron lifetime makes the electron diffusion to be easy due to their increased diffusion length. This results indicated that the Al₂O₃ /ZnO photoanode have higher electron transport and lower recombination rate at the photoanode-sensitizer-electrolyte interface and the same property leading to higher solar cell efficiency performance.

4 CONCLUSION

In our work, we exploit the mechanism, interaction of our compounds and reasoning clearly. After that, We show some theoretical aspects support to the experimental results to unveil the fundamental interaction between the interface of the solar cell. ZnO based photoanode material is sensitized by Pb-free methylammonium tin chloride.Among the four PSSCs,Al-doped ZnO with the CH₃NH₃SnCl₃ model have a higher efficiency performance (JSC=16.52MA, FF=73.0, PCE=9.41). By comparing all these structures, it can be concluded that the performance of Al-doped model

exhibit a better efficiency due to well adopted and successful combination with this sensitizer CH₃NH₃SnCl₃.This third generation solar cell is reasonably efficient and inexpensive.

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