Improved Efficiency of Ferroelectric Pb(Zr, Ti)O₃ (PZT) based Photovoltaic device with Colloidal Quantum Dots

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Abstract

Ferroelectric Pb(Zr, Ti)O₃ (PZT) thin films and PbS quantum dots (QDs) hybrid device are made for photovoltaic application, using a solution based fabrication process. The wide band gap of ferroelectric PZT can enable a high open circuit voltage. The colloidal PbS quantum dot provides a tailored absorption spectrum and an excellent light harvesting property, resulting in increased short circuit current. We present a hybrid photovoltaic device based on PZT thin film with a PbS quantum dot layer. With a combination of PZT and PbS QDs, the short circuit current has increased by 8000 times, while maximizing the open circuit voltage. The overall power conversion efficiency was 0.75 % and this is more than 50 times higher than a PZT film only photovoltaic device.

Keywords: Ferroelectrics, Solar energy materials, Electronic materials,

1. Introduction

Upon discovery of the ferroelectric photovoltaic effect,[1, 2] ferroelectric photovoltaic (PV) have attracted increasing interest.[3-5] Recent studies have reported that the power conversion efficiency (PCE) of ferroelectric PV devices can be considerably enhanced by engineering the ferroelectric domain architectures and interfaces.[3, 6, 7] However, the ferroelectric PV effect remained a scientific study rather than any application for PV devices, because of the low conductivity of ferroelectric materials and comparably poor PCE. There have been several reports that show improved photovoltaic properties using a hybrid approach with ferroelectric materials and organic/inorganic materials.[3, 8] There was a successful demonstration of efficient charge collection using a plasmonic-ferroelectric hybrid structure. Another study shows the importance of the internal electric dipole of ferroelectric materials that can manipulate collection of photocurrent.[9, 10] These works shows that the ferroelectric materials can boost the open circuit voltage of the photovoltaic device while increasing the short circuit current using a well matched light harvesting material.

Colloidal quantum dots offer several advantages for photovoltaic applications such as wide and tunable spectrum,[11, 12] low fabrication costs associated with solution processing,[13, 14] high electron mobility compared to polymer base PV,[15] broad absorption in the near-infrared,[16] and carrier multiplication.[17-19] PbS QDs have been well studied due to its broad spectrum for light harvesting.[15, 17, 20-23] PbS based photovoltaic device showed a great potential using surface treatment [24] or structure engineering, such as funnel structure[25] or energy bandgap engineering.[18, 26] However, the small bandgap of PbS QDs limits its open circuit voltage, which is typically less than 0.3 V.[27]

In this report, we present a new approach to fabricating a hybrid PV device using ferroelectric Pb(Zr, Ti)O₃ (PZT) and colloidal PbS QDs. Both PZT and PbS QDs can be prepared by chemical synthesis methods and they offer all solution based processes for device fabrication. This approach addresses the issues of poor light harvesting property of PZT and the small open circuit voltage of PbS PV device by

taking advantages of two different materials. Our novel hybrid structure demonstrates a great improvement in PCE compared to the conventional ferroelectric photovoltaic devices.

2. Methodology

To prepare PZT film, we chose a 2-methoxyethanol based sol-gel method, which has attracted due to its advantages of inexpensive, easy control of Zr and Ti ratio and control of hydrolysis.[28] And the PbS QDs were synthesized by a method similar to that described by Hines and Scholes.[16] The details of material preparation methods are discussed in supplementary contents.

For the fabrication of PZT/PbS-QDs hybrid photovoltaic devices, firstly, the prepared PZT sol-gel solution was spin-casted at 3500 rpm for 30 sec on a pre-cleaned Transparent Conducting Oxide (TCO) coated the glass. The coated PZT film was annealed at 600 °C for 15 min for crystallization. On top of the PZT layer, a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron PVP AI 4083) was spin-coated at 5000 rpm for 30 sec and it was baked at 120 °C for 30 min. Then, a PbS QD layer was spin-casted at 1500 rpm for 15 sec. The PbS film was treat by 1,2-ethanedithiol (EDT, 0.4 $\mu\text{l/ml}$ in acetonitrile) to ensure improved electrical conductivity. Finally, 100 nm-thick Al electrode was deposited using a thermal evaporator. The other reference devices with different film structures, TCO/PZT/Al and TCO/PbS/Al, were fabricated with the same method for each layer. All devices in this paper have the same active area of 0.06 cm^2 .

3. Results and Discussion

To confirm the perovskite structure of PZT thin film on TCO substrates, Indium Tin Oxide (ITO) or Fluorine doped Tin Oxide (FTO), XRD and P-E hysteresis were measured using a TCO/PZT/Al device. As shown in Figure 1 (a), we confirmed the crystalline structure of the PZT film on TCO. The bulk PZT powder (top) from the same sol-gel solution shows clear peaks. We also observed XRD peaks (middle

and bottom) from an 800 nm-thick and a 140 nm-thick PZT films on a FTO and ITO/glass substrates, respectively. The upper XRD pattern in Figure 1 (a) shows that (101) is the main peak from the PZT powders, which represent the crystal is rhombohedra structure (JCPDS card No. 70-4260).[29] The lower XRD pattern shows the main peaks with (100) and (101) which is the mixture of rhombohedra and tetragonal in the film. It should be noted that the weak XRD data is due to the very thin sample thickness. Although the PZT film on FTO substrate shows better XRD peaks, we choose PZT/ITO based devices due to its better electrical properties.

Inset of Figure 1(a) shows the P-E hysteresis from the PZT thin film on the ITO/glass substrate. Polarization is $0.9 \mu\text{C}/\text{cm}^2$, where the coercive field, E_c is 180 kV/cm. This result is comparable to the reported value in reference.[30] Both XRD and P-E hysteresis results confirm the perovskite PZT properties. Figure 1(b) shows the absorption spectrum of PbS quantum dots, and it shows the first excitonic absorption at 918 nm. The inset of Figure 1(b) shows the transmission electron microscopy image of the PbS quantum dots, and we measured the distance between the PbS atomic crystals, which is 2.95 Å from the inset of the high resolution TEM images. This reveals its high-crystalline nature and it is matched with bulk PbS crystal.[31]

Figure 2(a), (b) and (c) shows the absorption spectra and the external quantum efficiency (EQE) from PZT only, PZT/PbS-QD hybrid and PbS QD only devices, respectively. The PZT/PbS-QDs device consists of a 70 nm PZT thin film, a 70nm PEDOT:PSS and an 110 nm PbS QD film on transparent ITO coated glass (170nm). The transparent ITO layer serves as a window for the incident light and creates a Schottky barrier at the PZT/ITO interface.[32, 33] Since we use high temperature annealing process for PZT film, we carried out how the annealing temperature affect the ITO conductivity (Supplementary content). The other reference samples were fabricated under the same condition and compared. In Figure 2(a), due to the wide bandgap of PZT (3.1 eV) and poor electrical conductivity, the PZT only device shows a very low EQE value at its absorption spectrum. Figure 2(c) shows the measured data from PbS

only device and it shows well matched EQE corresponding to its excitonic peak at 970nm. The PZT/PbS-QDs hybrid device (Figure 2(b)) shows a similar EQE curve to the PbS only device. However, it has a reduction of EQE value in its shorter wavelength range. We believe the PZT layer absorbs most of the light at the shorter wavelength regime and these generate very small photocurrent current ($0.68 \mu\text{A}/\text{cm}^2$). However, one should note that the EQE extends to NIR, primarily due to the absorption of the PbS QDs. This shows that light absorbed by both PZT thin film (UV) and PbS QDs (NIR), contribute to the photocurrent.

Using the same devices, J-V (current density-voltage) characteristics were measured under AM1.5G illumination at $100 \text{ mW}/\text{cm}^2$. Figure 3(a) shows the best performing J-V characteristics of each device and it is summarized in Table 1. The PCE of the ferroelectric PZT the only device is comparably low as anticipated ($0.8 \times 10^{-4} \%$), and J_{sc} and V_{oc} were $0.68 \mu\text{A}/\text{cm}^2$ and 0.6 V with a fill factor (FF) of 18.5% , respectively. We believe that the lowest efficiency is originated from the limited light absorption due to its wide bandgap (3.1 eV) and the ferroelectric insulating property. The PbS QD only device shows 0.37% of PCE, with $J_{sc} = 10.6 \text{ mA}/\text{cm}^2$, $V_{oc} = 0.1 \text{ V}$ and a FF of 35.5% . It should be noted that the low efficiency compared to the best reported PbS the only device is due to the non-optimized device structure and the fabrication process. Compared to the PZT only device, the PZT/PbS-QDs hybrid device shows a significant increase of J_{sc} (from $0.68 \mu\text{A}/\text{cm}^2$ to $6.0 \text{ mA}/\text{cm}^2$), while not much degrading high V_{oc} . We achieved almost 4 orders of magnitude larger current than the PZT only device by taking advantages from ferroelectric PZT and PbS-QDs. The measured PCE was 0.75% and this corresponds to an improvement by more than 5 orders of magnitude compared to the best device based on a PZT only device, and by 60% to the PbS QD only device. Figure 3(b) shows the average values of V_{oc} and J_{sc} , with error bar from a dozen of devices. The average V_{oc} of PZT only, PZT/PbS hybrid and PbS only devices are $\sim 0.8 \text{ V}$, $\sim 0.4 \text{ V}$ and $\sim 0.2 \text{ V}$, respectively. And the average J_{sc} of PbS only, PZT/PbS hybrid and PZT only devices are $\sim 6 \text{ mA}/\text{cm}^2$, $\sim 0.35 \text{ mA}/\text{cm}^2$ and a few hundred nA/cm^2 respectively. Overall, we achieved a 0.75%

of PCE using the hybrid structure and it is more than 50 times larger value compared to the reported PCE from an ITO/PZT/Pt device (0.011%).[3]

Polarization dependency from the PZT film is an important charge transport mechanism of our device. We found that the internal polarization of the PZT film affects the photocurrent collection. As shown in Figure 3(c) and (d), there was a significant difference after the device was poled by applying +2V and -2V. The short circuit current extended from 4.1 mA/cm² to 4.9 mA/cm² after positive poling. The open circuit voltage is also decreased after the negative poling. Therefore, the internal polarization in the PZT film facilitates the charge transfer and it also affects the electronic band alignment. As shown in Figure 3(d), this was also observed in external quantum efficiency. After positive poling with a 2V of an external voltage, the quantum efficiency was increased while the opposite negative poling decreases the efficiency. The mechanism of power generation and polarization dependence are discussed in supplementary content.

4. Conclusion

In summary, we have introduced the PZT/PbS-QDs hybrid device as a novel architectural platform for ferroelectrics and solution-processed quantum dots optoelectronics and solar cells. Using solution based PZT thin film and PbS QDs, we demonstrated a simple and inexpensive fabrication method with improved photo-carrier efficiency. This approach enables to take advantages of ferroelectric PZT materials and PbS QDs for the high open circuit voltage and short circuit current, respectively. The hybrid device showed a significant improvement in short circuit current compared to PZT only device and achieved the best power conversion efficiency of 0.75 %.

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Figure 1. (a) XRD comparison between PZT crystalline powder, thin film on FTO/glass and ITO/glass substrate. Inset of (a) is the P-E Hysteresis form PZT thin film on ITO substrate. (b) Absorption spectra of PbS QDs, where the QD absorption peak is located at 918 nm. Inset of (b) is the TEM image of PbS QDs, which confirmed the size distribution of 3.4 – 4.0 nm scale and the atomic distance represents 2.95 Å.

Figure 2. External quantum efficiency (EQE) and absorption spectra for the (a) single layer PZT, (b) PZT/PbS-QDs hybrid and (c) single layer PbS-QD devices respectively. The hybrid device consists of PZT thin film and PbS quantum dots, which is ITO/PZT/PbS-QDs/Al structure.

Figure 3. J-V characterization of (a) PZT/PbS-QDs hybrid devices, and that of PZT, PbS-QDs for comparison. J-V characteristics measured in AM 1.5G solar simulated light for the best-performing results. (b) Plots of average values of Voc and Jsc by each device of PZT, PbS-QDs and PZT/PbS-QDs, with standard deviations. (c) I-V measurement data under dark and one sun illumination (AM1.5G 100mW) after +2V poling and -2V poling. (d) External Quantum Efficiency (EQE) spectra after +2V and -2V poling.

Table 1. Device performance for the best hybrid solar cells and respective reference devices

Device Structure	PZT Thickness [nm]	PbS Thickness [nm]	Voc [V]	Jsc [mA/cm ²]	FF	PCE
PbS	-	198	0.1	10.6	0.35	0.37%
PZT	140	-	0.6	0.00068	0.19	0.00008%
PZT/PbS	140	198	0.38	6.00	0.33	0.75%

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