

Preparation and characterization of NiO photocathodes sensitized with PbS quantum dots

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Abstract. The nanosized tremella-like NiO was synthesized by a simple hydrothermal method at low temperature. A novelty modified $(\text{CH}_3)_4\text{N}_2\text{S}/((\text{CH}_3)_4\text{N})_2\text{S}_n$ electrolyte was introduced in solar cell successfully and NiS as the counter electrode. Moreover, PbS sensitized p-type NiO was synthesized by chemical bath deposition (CBD) in an precursor solution to ensure the nanosized tremella-like NiO films obtain a better uniformity and high penetration. At the same time, a series of comparative experiments were designed for studying the influence of mesoporous NiO film thickness on the photoelectron characteristic of the cells. The result indicated that when there were three layers of screen printing and the thickness of NiO film was approximately $3\mu\text{m}$, the maximum power conversion efficiency of 0.87% was achieved, with 512 mV of V_{oc} , 0.33% of ff and 5.14 mA cm^{-2} of J_{sc} .

1. Introduction

Quantum dot sensitized solar cells (QDSSCs) exhibit many attractive features, including low production cost, high power conversion efficiency in theory and easy fabrication process, were considered as a good choice to be a substitute for dye-sensitized solar cells (DSSCs) [1, 2]. QDs are usually employed to construct n-type photoanodes where photocurrents owe to electrons injection into n-type semiconductor oxide [3, 4]. On the other hand, the possibility of using p-type photocathodes in solar cell was first reported in 1999 [5]. In addition, p-type photocathodes operate in an inverse mode, the holes are injected from a QDs into the valence band of the p-type semiconductor oxide when QDs are attached to hole acceptors [6, 7]. Nickel oxide (NiO) is attractive as electrode material in photovoltaic applications due to their good stability, a wide band gap and transparency [8, 9]. In the condition of solar cells, the major research of the p-type semiconductor materials that can be used as sensitized photocathodes is that they can be combined with n-type photoanodes in a tandem configuration. Such tandem solar cell, the maximum power conversion efficiency achievable increases from 30% for solar cell using a single junction to 42% when two semiconductors are employed [10]. Nevertheless, the photoelectron conversion efficiency of such tandem p-n solar cells have been

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hindered by the poor performance of the p-type photocathodes to date, resulting from the fact that the lower photocurrent of n-type and p-type solar cell [11, 12]. As a result, the photoelectron performances of the solar cell with the p-type photocathodes are significantly enhanced as a promising strategy to improve the photo-electrochemical characteristic of tandem p-n type solar cells [13]. Safarialamuti *et al.* prepared CdS/CdSe deposition onto mesoporous NiO films by successive ionic layer adsorption and reaction method (SILAR). Finally, the photoelectron conversion efficiency of 0.02% was obtained [14]. Subsequently, the conversion efficiency for CdSe sensitized p-type NiO solar cells to a best report of 0.35% has been reached by Park *et al* [13]. In 2016, Raissi *et al.* [15] have reported the fabrication of NiO-based QDSSCs using PbS QDs with a cobalt electrolyte and Pt counter. Finally the best conversion efficiency of solar cell achieved 0.4%.

In this paper, we synthesised the nanosized tremella-like NiO by a simple hydrothermal method at low temperature, and a series of comparative experiments were designed for studying the influence of mesoporous NiO film thickness on the photoelectron characteristic of solar cells. We assembled A novelty modified $(\text{CH}_3)_4\text{N})_2\text{S}/((\text{CH}_3)_4\text{N})_2\text{S}_n$ electrolyte was introduced in PbS sensitized p-type NiO solar cell successfully and NiS as counter electrode. The best efficiency of PbS sensitized NiO solar cells using polymer electrolyte and NiS counter electrode is 0.87% was obtained by the optimization of NiO film thickness. Moreover, a maximum IPCE value of solar cell was reached 32.7% at 340 nm.

2. Experimental Section

The tremella-like NiO were synthesized by simple hydrothermal method. In this process, 0.466 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 mL N, N-dimethylform (DMF), under magnetic stirring at room temperature to obtain a transparent solution. Then the prepared solution was poured into a 200 ml Teflon-lined stainless autoclave, which was kept at 80 °C for 20 h. A green-blue product was got, which was washed with deionized water and ethanol for several times, and dried in vacuum at 60 °C for 5 h. Finally, the black NiO was obtained through annealing at 500 °C for 3 h. Nanoporous NiO films were fabricated by screen printing an aqueous suspension of NiO nanoparticles on FTO conductive glass substrates and sintering at 500 °C for 30 min. CBD is considered as assemble PbS QDs deposited to the NiO photocathode. NiO films were modified by soaking in 0.1 M thioglycolic acid (TGA) for 1 min. Subsequently, the TGA-modified NiO film was soaked into an ethanol solution including 0.5 M $\text{Pb}(\text{NO}_3)_2$ for 1 min before cleaned by ethanol, and dried. Then after soaked for 1 min into a 0.5 M NaS solution, the sample was cleaned again with methanol. NiS as working electrode. Cleaned FTO glass was soaked into 0.5 M $\text{Ni}(\text{NO}_3)_2$ ethanolic solution for 30 s, cleaned by ethanol and dried. After the sample was soaked into 0.5 M Na_2S methanolic solution for 30 s, cleaned by methanol and dried. This process was continued five times to gain the NiS electrode. The modified electrolyte be made up of 0.01 M $((\text{CH}_3)_4\text{N})_2\text{S}$, 0.02 M 4-tert-butylpyridine (TBP), 0.02 M LiClO_4 , 0.002 M S, 3-Methoxypropionitrile (MPN) was employed as a solvent for the polysulfide electrolyte. The $((\text{CH}_3)_4\text{N})_2\text{S}$ was synthesised by heating $(\text{NH}_4)_2\text{S}$ and $((\text{CH}_3)_4\text{N})\text{OH}$ at 100 °C.

3. Results and Discussion

3.1 Analysis of SEM morphology

Figure 1 reveals the typical FESEM morphology of NiO nanoparticles, it is clear that the as-prepared NiO has a tremella-like architecture with a diameter ranging from 3 to 4 μm. These tremella-like NiO are constructed by some thin nanosheets with smooth surface and about 8 nm in thickness, which are formed a multi layered structure.

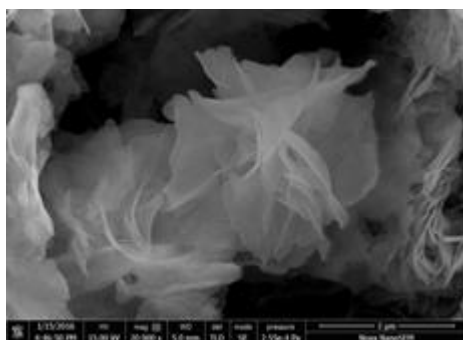


Figure 1. SEM images of tremella-like NiO

3.2 Analysis of XRD spectra

Figure 2 illustrates the typical XRD pattern of NiO/PbS composite and the pure NiO nanoparticles. As shown in Figure. 2a, the typical pattern peaks at 2θ values of NiO nanoparticles are approximately 37.24° , 43.15° , 62.58° and 75.26° , which correspond to (111), (200), (220) and (311) bunsenite planes of NiO, respectively(JCPDS card NO. 47-1049). In Figure. 2b, compared with the pattern of pure NiO nanoparticles, the diffraction peaks of the NiO/PbS are perfectly indexed as pure galena PbS phase (JCPDS card NO.05-0592). Furthermore, there are no clear peaks for impurity on the patterns, which indicates that the product is pure and other impurities were not generated during their processing.

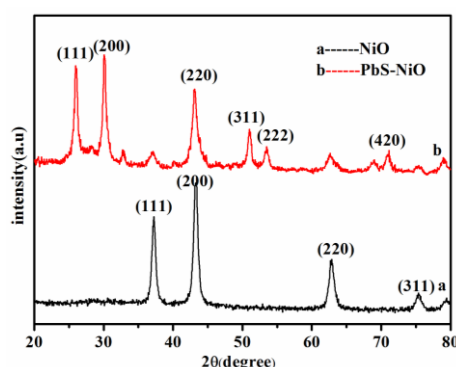


Figure 2. XRD spectra of NiO/PbS and pure NiO

3.3 J-V characteristics

The photocurrent-voltage (J - V) curves of the QDSSCs based on NiO with different thickness as shown in Figure 3. Key photoelectron characteristic parameters of solar cells are summarized in table 1. It can be obviously observed that with the increasing number of layers of screen printing, both J_{sc} and V_{oc} of the NiO/PbS solar cells slightly increase from 3.38 mA cm^{-2} and 191 mV for one layer to 5.14 mA cm^{-2} and 512 mV for three layers, respectively. A maximum efficiency of 0.87% are achieved for the solar cell with three layers of screen printing, and then decreases with a further increase in the number of layers. In present situation, the thickness of NiO film would increase after each layer. Such an increase layers of screen printing results in adsorbing more quantum dots, which is advantageous to increase the amount of collected holes and the efficiency of solar cell. However, the injection of the hole will be hampered with the sequentially increasing of film thickness, which is responsible for the reduce of J_{sc} and V_{oc} values.

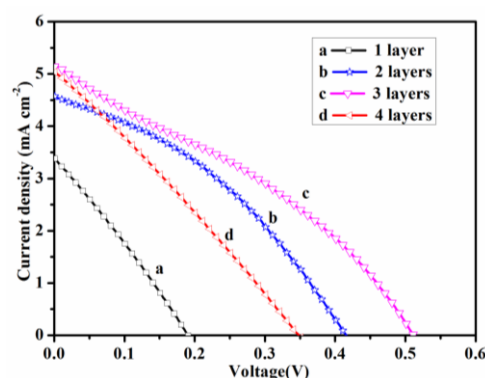


Figure 3. *J-V* spectrum of NiO with different layers

Table 1. Photoelectron characteristic of the QDSSCs measured under 1 sun illumination

Sample	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	Eff/%
1	0.191	3.38	0.27	0.18
2	0.416	4.57	0.37	0.70
3	0.512	5.14	0.33	0.87
4	0.349	5.04	0.27	0.48

3.4 IPCE spectrum

The incident photon to current efficiency (IPCE) spectra of a p-QDSSCs assembled from different thickness NiO thin film can be found in Figure 4. The IPCE spectra for three layers of screen printing displays much larger photo response at wavelengths below 420nm compared to one layer. The IPCE reached a maximum of 32.7% at 340 nm. The IPCE spectra was not enhanced with further increase in the NiO layer thickness. It can be reasonable as far as 30%-40% of the incident photons were absorbed by the NiO thin film over most of the visible wavelength range. Photocurrents were not observed due to photons were absorbed by the NiO thin film.

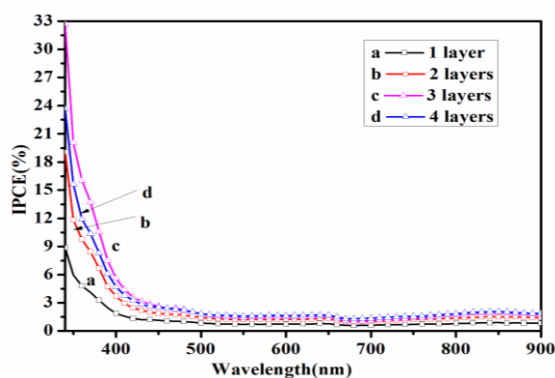


Figure 4. IPCE spectrum of NiO with different layers

4. Summary

In this paper, we have successfully synthesized tremella-like NiO by a simple hydrothermal method, and researched the influence of NiO thin film thickness on the photovoltaic performance of p-type QDSCs. We found that when the layers of screen printing were 3 and when the thickness of NiO thin film was about 3 μm , the conversion efficiency of 0.87% was achieved, with 512 mV of V_{oc} , 0.33% of ff and 5.14 mA cm⁻² of J_{sc} . At the same time, the IPCE reached a maximum of 32.7% at 340 nm. It was suggested that the p-type NiO/PbS structure could be successfully used to assemble p-type solar cell.

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References

- [1] Kamat P V 2008 *J. Phys. Chem. C* **112** 18737-53
- [2] Wang H, Bai Y S, Zhang H, Zhang Z H, Li J H and Guo L J 2010 *J. Phys. Chem. C* **114** 16451-5
- [3] Santra P K, Kamat P V 2012 *J. Am. Chem. Soc* **134** 2508-11.
- [4] Vasko J, Victoria G P, Sixto G, Eneko A, Germán C, Ramon T Z, Iván M S, Juan B 2011 *J. Am. Chem. Soc* **133** 20156-9
- [5] He J, Lindström H, Hagfeldt A, Lindquist S E 1999 *J. Phys. Chem. B* **103** 8940-3
- [6] Barceló I, Guillén E, Lana-Villarreal T, Gómez R 2013 *J. Phys. Chem. C* **117** 22509-17
- [7] Wang Z, Shakya A, Gu J, Lian S, Maldonado S 2013 *J. Am. Chem. Soc* **135** 9275-8
- [8] Nattestad A, Mozer A J, Fischer M K R, Cheng Y B, Mishra A, Bäuerle P, Bach U 2010 *Nat. Mater* **9** 31-5
- [9] Rhee J H, Lee Y H, Bera P, Seok S I 2009 *J. Chem. Phys. Lett* **477** 345-8
- [10] Vos A D 1980 *J. Phys. D App. Phys* **13** 839-46
- [11] Borgström M, Blart E, Boschloo G, Mukhtar E, Hagfeldt A, Hammarström L, Odobel F, 2006 *J. Phys. Chem. B* **109** 22928-34
- [12] Morandeira A, Fortage J, Edvinsson T, Pleux L L, Blart E 2008 *J. Phys. Chem. C* **112** 1721-28
- [13] Park M A, Lee S Y, Kim J H, Kang S H, Kim H 2014 *Mol. Cryst. Liq. Cryst* **598** 154-62
- [14] Safarlamuti A, Jennings J R, Hossain M A, Yung L Y L, Wang Q 2013 *Phys. Chem. Chem. Phys* **15** 4767-74
- [15] Raissi M, Pellegrin Y, Jobic S, Boujtita M, Odobel F 2016 *Sci. rep* **6**