ChemPubSoc Europe

DOI: 10.1002/slct.201702208

Chemistry SELECT Full Papers

Materials Science inc. Nanomaterials & Polymers

Facile In Situ Growth of Nanostructured Copper Sulfide Films Directly on FTO Coated Glass Substrates as Efficient Counter Electrodes for Quantum Dot Sensitized Solar Cells

Sarpangala Venkataprasad Bhat,*[a, b] Moorthy Dhanasekar,[a] Kelly M. Rickey,[b] and Xiulin Ruan[b]

We report a facile chemical solution deposition method for fabricating nanostructured copper sulfide film directly on fluorine doped tin oxide (FTO) coated glass substrates and demonstrate its use as efficient counter electrodes in quantum dot based solar cells. A typical quantum dot sensitized solar cell with CdS sensitized photo-anode using this counter electrode shows ~25% improvement in the power conversion efficiency when compared to the reference device assembled with conventional thermally evaporated gold/FTO counter electrode. The superior electrocatalytic activity of the copper sulfide electrode is also substantiated by potentiostatic I–V curves and electrochemical impedance spectroscopy.

Introduction

Solar energy harvesting is a highly sought after research area where nanostructured materials are proven to be beneficial due to their unique properties. One of the much pursued type of solar cells based on nanomaterials is quantum dot sensitized solar cells (QDSSCs). Owing to unique properties of semiconductor quantum dots, QDSSCs have the promise of low cost, easy fabrication, and better efficiency.[1] In a typical sensitized solar cell, a semiconductor metal oxide is sensitized by absorber, and the device is assembled using a counter electrode with an electrolyte in between as the redox couple. Counter electrodes facilitate the transfer of electrons from external circuit to the electrolyte and thus play a key role in catalyzing reduction of the redox electrolyte. Therefore, an ideal material for counter electrode should have high electrical conductivity, large surface area, and good catalytic activity.[2,3]

The counter electrode used in sensitized solar cells is generally a thermally evaporated platinum or gold film on FTO substrate. In the case of QDSSCs where polysulfide electrolyte is generally used as the redox couple, Au has been proven to be a better counter electrode along with its good catalytic properties.[3–5] For example,[3] the QDSSCs with CdS/CdSe quantum dots based on Au counter electrodes showed improved power conversion efficiencey (~ 4.2%) as compared to the device based on Pt electrode (~3.7%). Further studies in search for simpler and inexpensive efficient materials for the counter electrode have shown that, the transition metal chalcogenide such as copper sulfide is more stable and exhibit superior electrocatalytic activity for polysulfide reduction.[6] Thus recently there have been many studies on new counter electrode materials in QDSSCs based on these metal chalcogenides and their carbon based composite materials.[7–21] The studies indicated that naoparticulate films or composites of binary, ternary and quarternary compounds based on copper sulfide are promising candidates for the replacement of expensive noble metals in counter electrodes of QDSSCs.

A common method to fabricate the copper sulfide counter electrodes for QDSSCs is exposing Cu brass to sulfide solution after acid treatment to obtain an interfacial layer of metal sulfide. To overcome the problem of continual corrosion and mechanical instability associated with this method, newly explored methods use screen-printed Cu_2S combined with conductive carbon[8] and Cu_2S- reduced graphene oxide composite.[9] There are reports on the copper sulfide counter electrodes prepared either by vacuum thermal evaporation, successive ionic layer adsorption and reaction or by coating of pre synthesized particles of metal chalcogenides.[10–15] Recently, combination of chemical bath deposition method with $TiCl_4$ treatment has been explored to develop more efficient copper sulfide counter electrodes for QDSSCs.[16] Other methods such as electroplating of copper followed by reaction with polysulfide solution also resulted in efficient counter electrodes as compared to the brass based electrodes.[17,18] Copper sulfide with nanosheet structure synthesized on copper (Cu) film coated FTO glass has been explored as the counter electrode for bifacial QDSSCs.[19] Hierarchical Cu_7S_4 nanotubes assembled by hexagonal nanoplates using an in-situ growth route and etching process have been reported.[20] In situ growth of CuS and $Cu_{1.8}S$ nanosheet arrays via solvothermal process with seeded FTO coated glass and their use as efficient counter electrodes for QDSSCs was also reported.[21]

However, strategies to form the copper sulfide films in situ directly on the FTO coated glass as counter electrode in

---

[a] Dr. S. V. Bhat, M. Dhanasekar
SRM Research Institute, Department of Physics & Nanotechnology, SRM University, Kattankulathur-603203, Tamil Nadu, India
E-mail: venkataprasad.b@res.srmuniv.ac.in
[b] Dr. S. V. Bhat, Dr. K. M. Rickey, Dr. X. Ruan
Birck Nanotechnology Center & School of Mechanical Engineering, Purdue University, West Lafayette, IN 47906, USA.

Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.201702208

QDSSCs are quite limited, while such methods will help to achieve low cost large scale production of the devices. Moreover, most of these earlier studies have compared the performance of new materials for counter electrode to Pt as the reference material in QDSSCs or DSSC (Dye sensitized solar cell) s. For example, Mulmudi et. al.[22] reported the in-situ prepared copper sulfide on FTO via the decomposition of spin coated precursor solution and showed its superioirity in comparison with FTO/Pt counter electrodes in DSSCs. As explained above, the Au based electrodes outperform Pt for the redox reaction involving the polysulfide electrolyte in QDSSCs[3–5] and hence a comparison with FTO/Au would be sought by the QDSSC researchers. In this communication, we explore the use of a simpler method employing the decomposition of doctor blade coated precursor paste at low temperature, to fabricate the nanostructured copper sulfide counter electrode directly on the FTO coated glass substrates and compare its performance to that of the commonly used FTO/Au film electrode in a typical QDSSC device.

Results and Discussion

Copper sulfide films were formed in situ on the substrates via decomposition of the coated precursor paste. Figure 1 shows the XRD pattern of the as prepared copper sulfide film. The phases were identified as covellite (CuS, JCPDS # 06–0464) and digenite ($Cu_{1.8}S$, JCPDS # 85–1693), with covellite as the dominant phase. Earlier reports on solution based synthesis of copper sulfide nanostructures also showed the presence of the mixture of covellite and digenite phases for the temperature range used for the synthesis.[23 – 25]

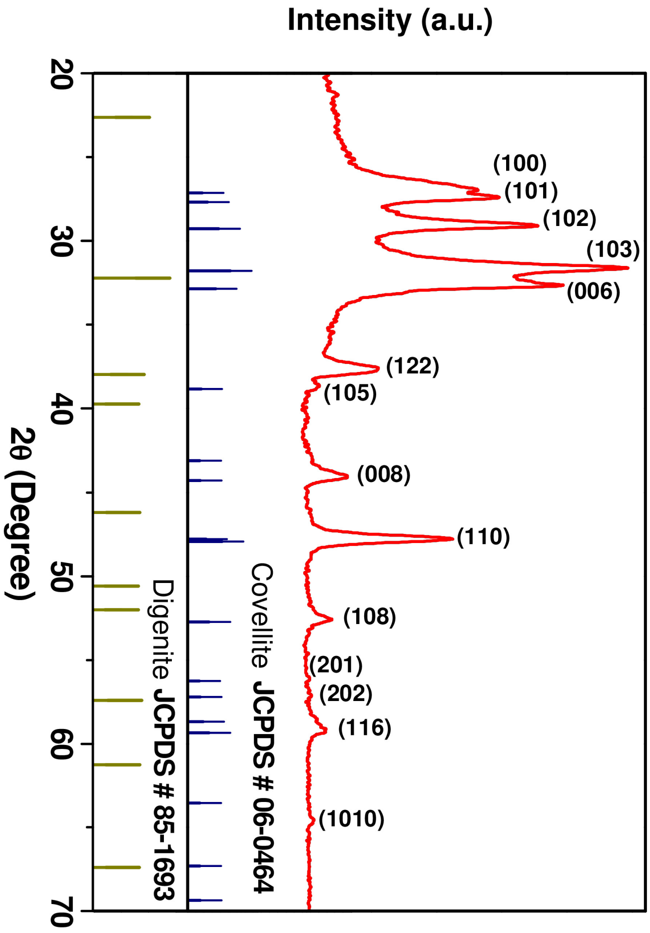

Figure 1. XRD pattern of the copper sulfide film.

The average composition of the copper sulfide film obtained by EDS analysis (Figure 2) was found to be $Cu_{1.7}S$, which is also consistent with the mixed phases of deginite and covellite.

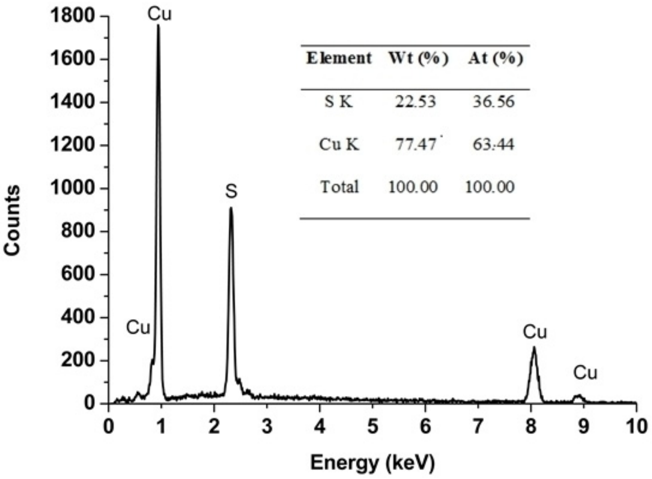

Figure 2. EDAX spectrum of the copper sulfide film.

Figure 3 is a typical FESEM image of the copper sulfide film. The FESEM images showed that the dense film was made of

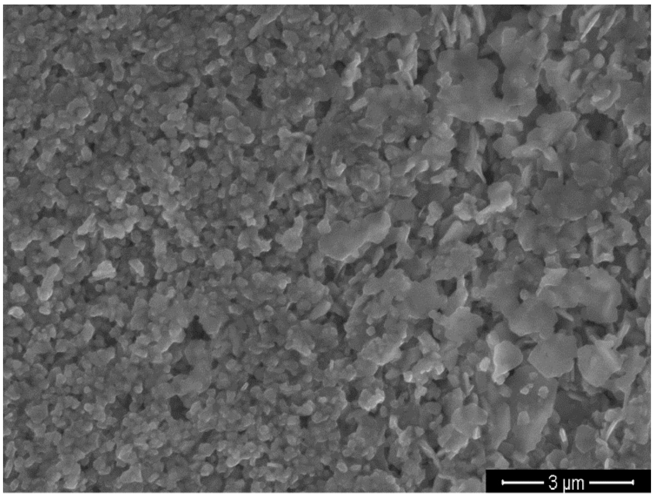

Figure 3. FESEM image of the copper sulfide film.

nanostructures of size in the range of 100–200 nm. The Raman spectrum (Figure 4) of the film showed an intense peak around 470 cm^{-1} which can be assigned to the generally observed Raman signature of CuS phase.[18,26] The digenite and other phases of copper sulfide have no reported Raman signatures, thus we have only peaks corresponding to the covellite phase.

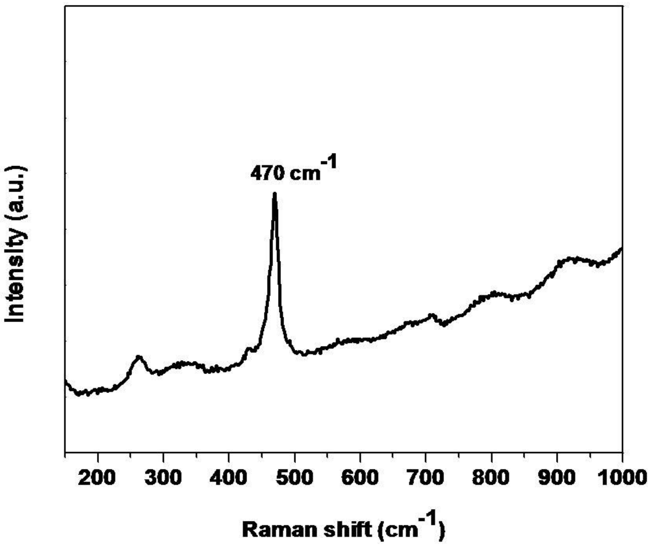

Figure 4. Raman spectrum of the copper sulfide film

The obtained carrier concentration (P), hall coefficient (R_H), mobility (μH), and the resistivity of the film are tabulated in Table 1. As deposited copper sulfide thick film showed a positive hall coefficient, confirming the p-type nature of the sample.[27] The obtained value of the carrier concentration was ~10^{19} cm^{-3}, which is comparable with the earlier reports[28,29] confirming the thick film to be semiconducting in nature. Mobility and the conductivity of the as-deposited copper sulfide film were higher as compared to many of the previous reports.[29–33] This enhanced electron transport may be due to many factors including the crystal structure and the presence of nanostructured channels in the film well connected to each other.

Several QDSSCs devices were fabricated with the copper sulfide counter electrode prepared as above. A typical photocurrent density (J) vs. photovoltage (V) curve for the QDSSCs fabricated is shown in Figure 5. For comparison, similar device was fabricated with FTO/Au as the counter electrode. The photovoltaic parameters extracted from the J–V curves are tabulated in Table 2. The device with FTO/copper sulfide film as the counter electrode showed an improved efficiency of 1.16% as compared to 0.93% from that with FTO/gold film as the counter electrode. The improvement in the efficiency (~25% increase) is mainly due to the increased fill factor (FF) and the short circuit current density (Jsc), although there is slight decrease in the open circuit voltage (Voc).

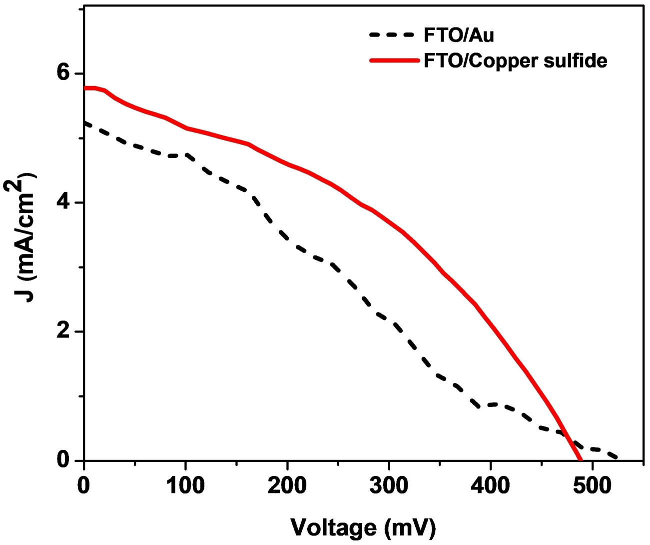

Figure 5. Current - voltage characteristics under illumination of AM1.5, for a typical quantum dot sensitized solar cell with counter electrode made of FTO/Au film (dashed black) and FTO/copper sulfide film (solid red).

Table 2. The equivalent circuit fitting parameters for the Nyquist plots from electrochemical impedance spectroscopy and photovoltaic parameters of tested QDSSCs, with the FTO/copper sulfide and FTO/Au counter electrodes.

Counter electrode	R_s [Ω]	R_{ct} [Ω]	CPE [μF]	J_{sc} [mA/cm^2]	V_{oc} [V]	FF	Eff (%)
Au	5	1565	29.8	5.20	0.52	0.27	0.93
Copper sulfide	27	441	1750	5.84	0.49	0.40	1.16

Table 1. Electrical properties of the as prepared copper sulfide thick film in comparison with other reports in literature.

Method	Carrier concentration (P) [cm^{-3}]	Mobility (μ_H) [cm^2/Vs]	Resistivity (ρ) [Ω cm]	Hall coefficient (R_H) [cm^3/C]	Reference
Doctor blade coating	1.56×10^{19}	13.23	3.51×10^{-3}	35.82	This work
CBD	5.76×10^{17}	0.32		11.06	29
Dip coating	2.23×10^{17}	0.58		31.46	29
RF sputtering	1×10^{16}–3×10^{19}	4–10	0.8–0.04		28
Spray pyrolysis	1.50×10^{21}	18–25			30
MOCVD	1.22×10^{12}	16.3	~3×10^5	10^5–10^6	32
CBD	3.43×10^{20}	47.3	3.85×10^{-4}	–	33
CBD	6.25×10^{18}–1.37×10^{21}	0.17–3.5	0.82–0.02		34

The potentiostatic I–V curves in Figure 6 show that the FTO/copper sulfide electrode provided about 10-fold increase in current density as compared to the FTO/gold electrode, at 0.5 V in the cathodic direction. This indicates the superior electrocatalytic ability of the copper sulfide based electrode.

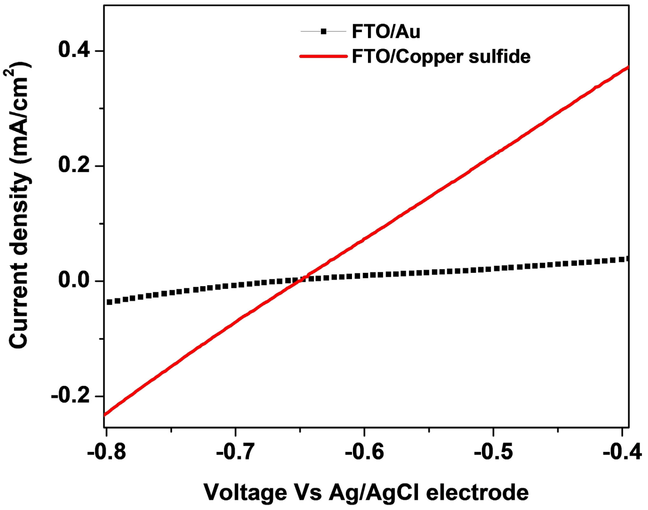

Figure 6. Potentiostatic I–V curves of FTO/Au and FTO/copper sulfide working electrodes (with an Ag/AgCl reference electrode and Pt counter electrode).

Figure 7 shows Nyquist plots measured for the symmetric cells made of FTO/Au and FTO/copper sulfide electrodes filled with polysulfide redox electrolyte under same experimental conditions. An equivalent circuit having a series resistance R_s with a parallel combination of electron transfer resistance (R_{ct}) and constant phase element/capacitance (CPE) for the counter electrode-electrolyte interface is used for fitting the plots. The values of R_s, R_{ct} and CPE obtained by fitting the equivalent circuit for the Nyquist plots are included in Table 2. The low R_{ct} of copper sulfide concurs well with the potentiostatic I–V plot indicating its superior catalytic activity during the electron transfer process. The higher value for the capacitance is the result of higher surface area, which again contributes to the better catalytic activity.

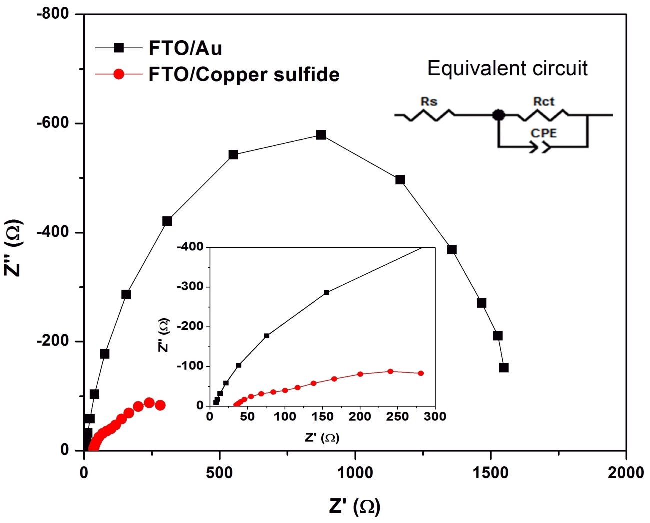

Figure 7. Nyquist plots of the symmetric cells with FTO/Au and FTO/copper sulfide electrodes. Inset: Inset: Equivalent circuit for fitting the EIS and the rescaled plot showing the high frequency range; Rs: serial resistance; Rct: electron transfer resistance; CPE: Constant Phase Element.

The increased J_{sc} and FF resulting in the higher efficiency obtained for the solar cell with FTO/copper sulfide counter electrode, can be explained on the basis of its electro-catalytic properties. Higher J_{sc} and FF generally correspond to a smaller series resistance of the solar cell device. The total series resistance of a photoelectrochemical solar cell can be expressed as the sum of substrate resistance, electron transfer resistance (R_{ct}) and the diffusion impedance in the electrolyte.[12] Thus, the smaller R_{ct} of the FTO/copper sulfide counter electrode, as described above, will contribute to the smaller series resistance of the device, resulting in higher J_{sc} and FF. This corresponds to the superior electroctalytic ability and higher electrolyte reduction rate on the surface of the electrode.

Conclusions

In conclusion, a simple solution based method was used to prepare nanostructured copper sulfide film on a FTO substrate for the application as counter electrode in a QDSSC. Conversion efficiency of 1.16% was obtained as compared to 0.93% from standard QDSSCs fabricated with FTO/Au as counter electrode. The simple method for the fabrication of FTO/copper sulfide counter electrode is promising for low cost large scale manufacturing of the QDSSCs and also can be extended to other metal chalcogenide compounds to be used as counter electrode materials.

Supporting Information Summary

Experimental details are provided as the supporting information.

Acknowledgements

SVB, KR and XR would like to acknowledge the partial support by the National Science Foundation, USA (Award # CBET-0933559). SVB and MD would like to acknowledge the financial support from the SRM University, DST-SERB (ECR/2015/000513) and MNRE (31/03/2014-15/PVSE-R&D), Government of India. Authors also thank Dr. Ramesh Babu, Bharathidhasan University, Trichy for the help with Hall effect measurements.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Electrochemistry · Energy Conversion · Nanostructured films · Quantum dots · Synthetic methods

[1] P. V. Kamat, *J. Phys. Chem. Lett.* **2013**, *4*, 908–918.
[2] Z. Yang, C. Y. Chen, P. Roy, H. T. Chang, *Chem. Commun.* **2011**, *47*, 9561–9571.
[3] Y. L. Lee, Y. S. Lo, *Adv. Funct. Mater.* **2009**, *19*, 604–609.
[4] I. Mora-Sero, S. Gimenez, T. Moehl, F. Fabregat-Santiago, T. Lana-Villareal, R. Gomez, J. Bisquert, *Nanotechnology* **2008**, *19*, 424007.
[5] M. Seol, H. Kim, Y. Tak, K. Yong, *Chem. Commun.* **2010**, *46*, 5521–5523.
[6] G. Hodes, J. Manassen, D. Cahen, *J. Electrochem. Soc.* **1980**, *127*, 544–549.
[7] M. Deng, Q. Zhang, S. Huang, D. Li, Y. Luo, Q. S. T. Toyoda, Q. Meng, *Nanoscale Res. Lett.* **2010**, *5*, 986–990.
[8] M. H. Deng, S. Q. Huang, Q. X. Zhang, D. M. Li, y. H. Luo, Q. Shen, T. Toyoda, Q. B. Meng, *Chem. Lett.* **2010**, *39*, 1168–1170.
[9] J. G. Radich, R. Dwyer, P. V. Kamat, *J. Phys. Chem. Lett.* **2011**, *2*, 2453–2460.
[10] Z. Yang, C–Y. Chen, C–W. Liu, C–L. Li, H–T. Chang, *Adv. Energy Mater.* **2011**, *1*, 259–264.
[11] S. Wang, W. Dong, X. Fang, S. Zhou, J. Shao, Z. Deng, R. Tao, Q. Zhang, L. Hu, J. Zhu, *Electrochim. Acta* **2015**, *154*, 47–53.
[12] J. Xu, X. Yang, T. L. Wong, C. S. Lee, *Nanoscale* **2012**, *4*, 6537–6542.
[13] Y. Cao, Y. Xiao, Jin-Young Jung, Han-Don Um, Sang-Won Jee, H. M. Choi, J. H. Bang, Jung-Ho Lee, *ACS Appl. Mater. Interfaces* **2013**, *5*, 479–484.
[14] S. Gimenez, I. Mora-Sero, L. Macor, N. Guijarro, T. Lana-Villarreal, R. Gomez, L. J. Diguna, Q. Shen, T. Toyoda, J. Bisquert, *Nanotechnology* **2009**, *20*, 295204.
[15] Z. Yang, C. Y. Chen C. W. Liu, H. T. Chang, *Chem. Commun.* **2010**, *46*, 5485–5487.
[16] J. Xu, J. Xiao, J. Dong, Y. Luo, D. Li, Q. Meng, *Electrochim. Acta* **2014**, *127*, 180–185.
[17] K. Meng, P. K. Surolia, O. Byrne, K. R. Thampi, *J. Power Sources* **2014**, *248*, 218–223.
[18] K. Zhao, H. Yu, H. Zhang, X. Zhong, *J. Phys. Chem. C* **2014**, *118*, 5683–5690.
[19] W. Ke, G. Fang, H. Lei, P. Qin, H. Tao, W. Zeng, J. Wang, X. Zhao, *J. Power Sources* **2014**, *248*, 809–815.
[20] M. Wang, W. Chen, J. Zai, S. Huang, Q. He, W. Zhang, Q. Qiao, X. Qian, *J. Power Sources* **2015**, *299*, 212–220.
[21] M. Ye, X. Wen, N. Zhang, W. Guo, X. Liu, C. Lin, *J. Mater. Chem. A* **2015**, *3*, 9595–9600.
[22] H. Mulmudi, S. K. Batabyal, M. Rao, R. R. Prabhakar, N. Mathews, Y. M. Lam, S. G. Mhaisalkar, *Phys. Chem. Chem. Phys.* **2011**, *13*, 19307–19309.
[23] L. Isac, I. Popovici, A. Duta, *Rev. Roum. Chim.* **2011**, *56*, 1107–1112.
[24] S. A. Patil, N. Mengal, A. A. Memon, S. H. Jeong, H. S. Kim, *J. Alloys Compd* **2011**,*708*, 568–574.
[25] T. Safrani, J. Jopp, Y. A. Golan, *RSC Adv.* **2013**, *3*, 23066–23074.
[26] E. Rudigier, B. Barcones, I. Luck, T. Jawhari-Colin, A. Perez-Rodrıguez, R. Scheer, *J. Appl. Phys.* **2004**, *95*, 5153–5158.
[27] S. D. Sartale, C. D. Lokhande, *Mater. Chem. Phys.* **2000**, *65*, 63.
[28] Y. B. He, A. Polity, I. Osterreicher, D. PFisterer, R. Gregor, B. K. Meyer, M. Hardt, *Phys. B* **2001**, *1069*, 308–310.
[29] S. H. Chaki, M. P. Deshpande, J. P. Tailor, *Thin Solid Films* **2014**, *550*, 291.
[30] M. Adelifard, H. Eshghi, M. M. B. Mohagheghi, *Appl. Surf. Sci.* **2012**, *258*, 5733.
[31] M. Adelifard, H. Eshghi, M. M. B. Mohagheghi, *Bull.Mater.Sci.* **2012**, *35*, 739.
[32] S. K. Maji, N. Mukherjee, A. K. Dutta, D. Srivasta, P. Paul, B. Karmakar, A. Mandal, B. Adhikary, *Mater. Chem. Phys.* **2011**, *130,* 392.
[33] N. K. Allouche, T. B. Nasr, C. Guasch, N. K. Turki, *Comptes Rendus Chimie.* **2010**, *13*, 1364–1369.
[34] J. S. Cruz, S. A. Mayén Hernández, F. P. Delgado, O. Z. Angel, R. C. Pérez, G. T. Delgado, *Int. J. Photoenergy* **2013**, *2013*, Article ID 178017.

Submitted: September 20, 2017
Revised: November 2, 2017
Accepted: November 6, 2017