Materials Letters 185 (2016) 584–587

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Produce of graphene/iron pyrite (FeS_2) thin films counter electrode for dye-sensitized solar cell

Bayram Kilic [a,*], Sunay Turkdogan [a], Oguz Can Ozer [a], Mansur Asgin [a], Ozge Bayrakli [b], Gokhan Surucu [c], Aykut Astam [d], Duygu Ekinci [e]

[a] Department of Energy Systems Engineering, Faculty of Engineering, Yalova University, 77100 Yalova, Turkey
[b] Middle East Technical University, Department of Physics, 06800 Ankara, Turkey
[c] Ahi Evran University, Kaman Vocational College, 40100 Kirsehir, Turkey
[d] Department of Physics, Faculty of Science and Art, Erzincan University, Erzincan 24100, Turkey
[e] Department of Chemistry, Faculty of Sciences, Ataturk University, 25240 Erzurum, Turkey

ARTICLE INFO

Article history:
Received 7 April 2016
Received in revised form
13 May 2016
Accepted 17 June 2016
Available online 21 June 2016

Keywords:
Graphene
Tio_2
DSSC
Pyrite (FeS_2)
Counter electrode

ABSTRACT

Dye-sensitized solar cells (DSSCs) provide a low cost alternative to the conventional solar cells due to their easy and inexpensive device fabrication steps. Generally, F:SnO_2 (FTO) conductive glass with a thin layer coating of platinum (Pt) is used as a counter electrode (CE) in DSSCs. Since Pt is rare and therefore expensive metal, we were looking for a way to produce a new counter electrode based on graphene/iron pyrite (FeS_2) thin films as an alternative to the Pt:FTO. In combination with a TiO_2 mesoporous photo-anode and an I_3^-/I^- redox electrolyte, graphene/FeS_2 CE based DSSC shows $\eta = 7.43\%$ energy conversion efficiency under 1 sun illumination (100 mW/cm^2, AM 1.5G) which is approximately 16.1% higher than conventional Pt CE ($\eta = 6.40\%$). External Quantum Efficiency (EQE) is found to be shifted upward when graphene/FeS_2 is used as CE in the place of Pt CE. The excellent performance of the graphene/FeS_2 CE makes it a very promising alternative to costly Pt in DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been intensively studied with a growing demand for potential alternatives for the next generation solar cells due to their low production cost, easy processing, relatively high energy conversion efficiency and eco-friendly fabrication steps [1]. A typical DSSC consists of a photo-anode, I^-/I_3^- redox electrolyte and Pt coated FTO counter electrode (CE) [2]. Counter electrode (CE) plays a vital role in order to increase the solar conversion efficiency of DSSCs. In standard DSSCs, a platinum-coated fluorine doped tin oxide (Pt:FTO) is usually used as CE because of their excellent catalytic activity and high electrical conductivity [3]. Although Pt gives a good performance, Pt sources are rare and thus leading to high cost in DSSCs [4]. Carbon based CE such as graphene, on the other hand, is a cheaper alternative, but it performs poorly as a CE [5]. In this study, we demonstrate for the first time that graphene based iron pyrite FeS_2 thin films exhibits a high specific surface area which is beneficial for the catalytic reaction and for the solar power conversion efficiency. Iron Pyrite FeS_2 with a suitable optical band gap energy of 0.95–1.5 eV has attracted much interests in both fundamental research and practical applications due to its inherent advantages such as excellent photo absorption with a large absorption coefficient, environmentally friendly, high electron mobility, non-toxic and high quantum efficiency ($>80\%$) [6,7]. In this paper, the graphene/FeS_2 CE was employed to investigate its effect on DSSCs' performance. The influence of graphene/FeS_2 CE on solar conversion efficiency in DSSC is compared with a conventional Pt CE. We introduce that the graphene/FeS_2 CE enable increase of the performance of the devices.

2. Experimental

TiO_2 mesoporous film was deposited on a FTO substrate by hydrothermal method using the same procedure presented in our previous work [8]. After the photo-anode is prepared, graphene was synthesized from graphite powder (Alfa Aesar, 325mesh, 99.9995%) by the modified Hummers method to form the counter electrode. After that, graphene layer was transferred onto another FTO substrate by deep coating method. $FeCl_3.6H_2O$ (Sigma-Aldrich) and Sulfur powder (%99.98) were used as precursors. 0.3 g iron chloride and 0.1 g sulfur were prepared in 40 ml DI water. The pH of the mixture was adjusted to 11 by Ammonia (%28). The

* Corresponding author.
E-mail addresses: bkilic@yalova.edu.tr, kbayramkilic@gmail.com (B. Kilic).

http://dx.doi.org/10.1016/j.matlet.2016.06.069
0167-577X/

solution was kept under magnetic stirring for 1 h. The mixture with immersed graphene/FTO substrate was placed and sealed in a Teflon-lined stainless steel autoclave and then heated to 175 °C and kept there for 8 h. The thin films, FeS_2 (pyrite), was obtained on the graphene/FTO substrate and washed with distilled water and ethanol several times to remove the excess polymer and ions, and finally dried at 75 °C for 6 h in a vacuum oven. In the last step, the film was sulfurized at 400 °C for 1 h in nitrogen atmosphere.

Hybrid DSSCs were prepared by adsorption of N719 dye molecules onto the surfaces of the prepared photoanodes (TiO_2 mesoporous film) for 6 h. This process was done by immersing the substrates in a 0.5 mM solution of the N719 dye, but beforehand the substrates were heated to 100 °C for 30 min. After 6 h, the samples were taken out, rinsed with acetonitrile and blow dried with nitrogen gas. The dye-sensitized TiO_2 and graphene/FeS_2 CE were sandwiched together using a 20 μm thick transparent Surlyn film (Meltonix 1170, Solaronix). The electrolyte consisting of 0.5 M tetrabutylammonium iodide, 0.05 M I_2 and 0.5 M 4-tertbutylpyridine in acetonitrile, was introduced between two electrodes using the capillary action. The active area of the cells was typically 0.25 cm^2.

3. Results and discussion

The TiO_2 mesoporous film was prepared by hydrothermal method as described in the experimental section. As seen on the SEM image in Fig. 1(a), homogenously distributed TiO_2 mesoporous structures were obtained on a FTO substrate with 20–100 nm pore radius. X-ray diffraction analysis exhibits strong diffraction peaks matching with TiO_2 anatase structures (Fig. 1(c)). The EDAX measurement confirms the presence of Ti and O atoms in the sample (Fig. 1(b)). Raman spectrum indicates that the bounds at 425, 542 and 666 cm^{-1} corresponded to the $B_{1g(1)}$, $A_{1g}+B_{1g(2)}$ and $E_{g(2)}$ modes of anatase, respectively.

The SEM AFM images and XRD, Raman spectrums of pure reduced graphene oxide (RGO) are shown in Fig. 2(a-f). The SEM and AFM images show pure graphene layer on the substrate. The XRD pattern of RGO exhibit a strong (002) diffraction peak at 29° and a (100) diffraction peak at 35°. Raman spectra confirms the formation of RGO as seen in Fig. 2(f). Two peaks around 1340 and 1610 cm^{-1} are respectively assigned to the characteristic D-band and G-band of graphene. FeS_2 were grown on a graphene/FTO substrate to form a new CE. The SEM and AFM images of graphene/FeS_2 thin film shows the cubic shape and good uniformity of the structures after annealing at 400 °C for 30 min (Fig. 2(a-d)). As seen in the SEM images, graphene/FeS_2 thin film shows nanoparticle size ranging between 20–50 nm and homogenous distribution on the substrate. The XRD diffraction peaks (Fig. 2(e)) can be indexed as a graphene/pyrite cubic phase of FeS_2 (JCPDS no 42-130), and no obvious impurity related peaks were observed. The sharp peaks in the XRD pattern suggest the excellent crystallinity of the as-grown graphene/FeS_2 thin films. Fig. 2(f) shows the Raman peaks at wavenumbers of 250, 320 and 440 cm^{-1} which correspond to the characteristic active modes of FeS_2 due to the Eg and in phase stretching vibration of Ag, respectively. In the Eg mode, S atoms are replaced vertically to the dimer axes. The peak around 530 cm^{-1} corresponds to the coupled vibration and stretching (Tg) modes or their combination. In addition, two Raman active band around 1344 cm^{-1} and 1735 cm^{-1} confirm D-

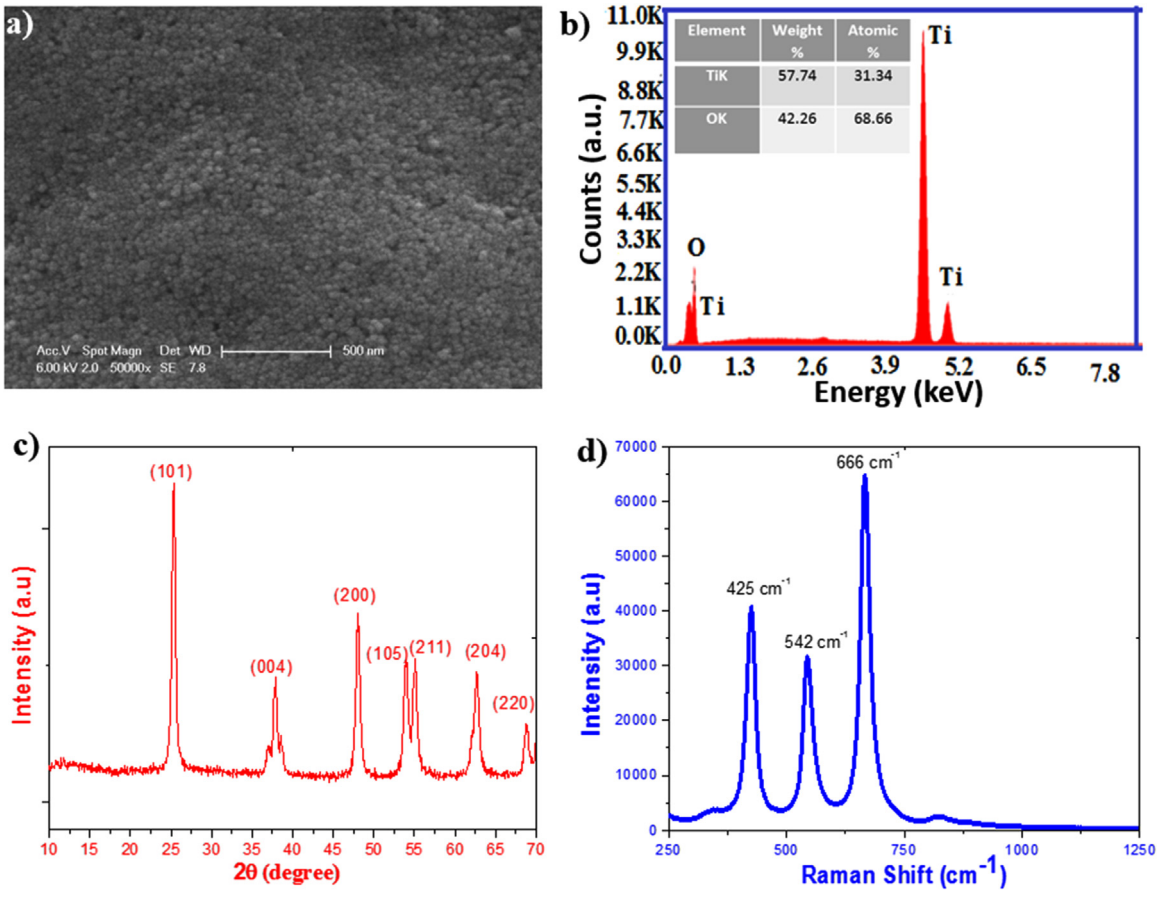

Fig. 1. Structural and optical characterizations of TiO_2 mesoporous structures (a) SEM images (b) EDAX measurement result (c) XRD pattern (d) Raman spectra taken from the TiO_2 sample.

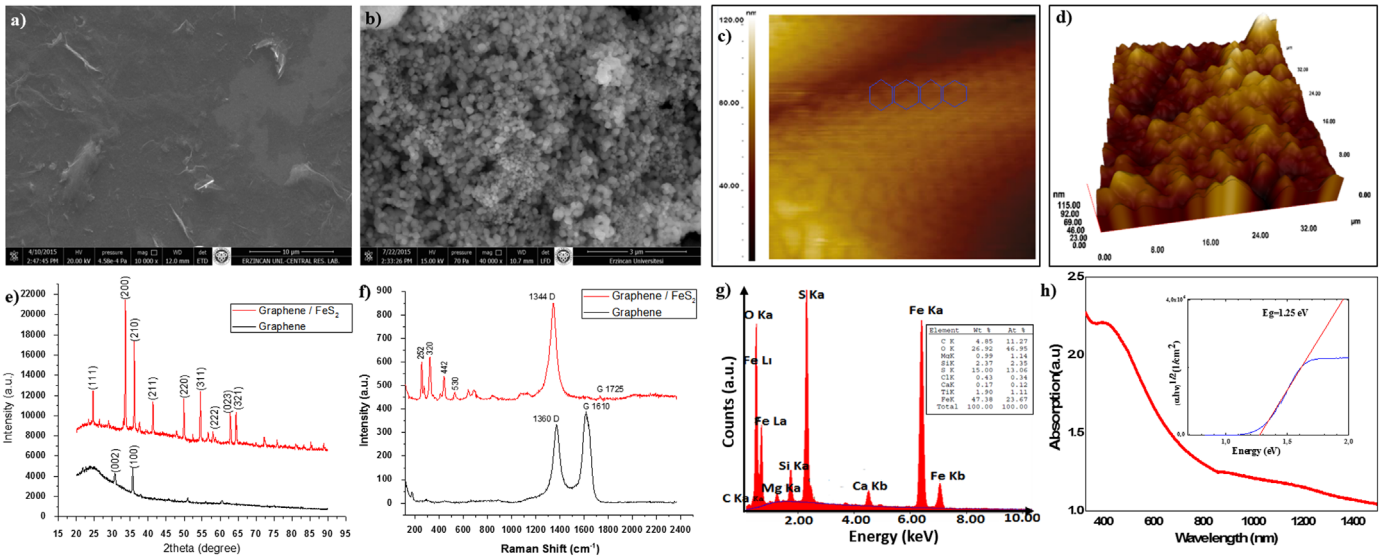

Fig. 2. (a-b) SEM, (c-d) AFM images and (e) XRD, (f) Raman analysis results of Graphene and Graphene/FeS_2samples. (g) EDAX and (h) UV–vis absorption analysis results of Graphene/FeS_2 counter electrode.

and G-bands of RGO. The optical properties of the graphene/FeS_2 were investigated by UV–Vis spectroscopy and the result is shown in Fig. 2(h). The optical band gap value of graphene/FeS_2 thin film wase obtained as 1.25 eV. UV–vis spectra indicates that the iron pyrite thin films with high density of grain boundaries can create strong photon scattering at interfaces and thus causing the high optical absorption. The EDAX analysis of the film shows the presence of Iron, Sulfur and Carbon atoms (Fig. 2(g)).

Fig. 3(a) and (b) show the schematic band and structure diagram of the produced DSSC, respectively, and those indicate the optimum work function and quick electron injection process. The current density-voltage characteristic of a graphene/FeS_2 CE based

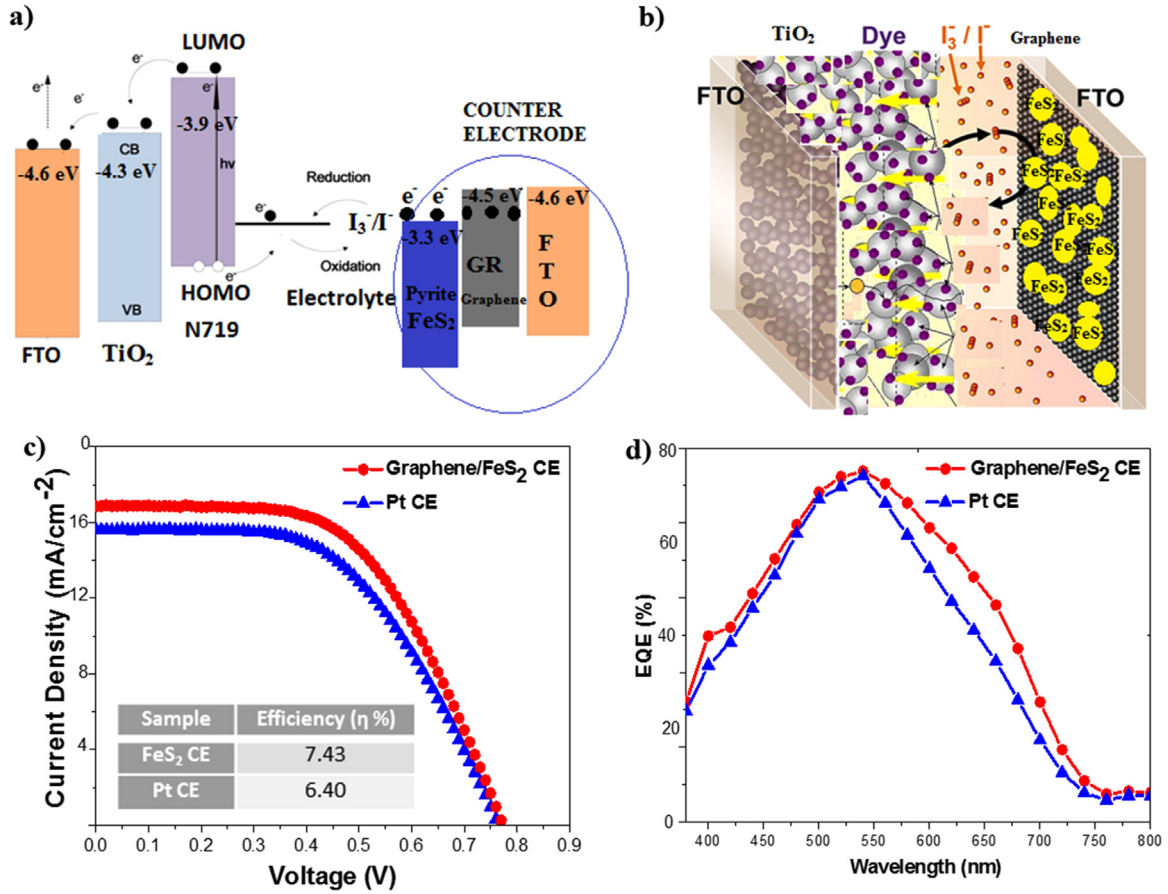

Fig. 3. (a)Schematic view of the band alignment of a Graphene/FeS_2 CE based DSSC (b) Schematic view of the cell structure (c) Current density-voltage (J-V) characteristics of dye-sensitized solar cells with graphene/FeS_2 thin films (about 1 μm thick) as CE, measured under AM 1.5G 1-Sun solar irradiance (100 mW/cm^2) (d) External Quantum Efficiency (EQE) spectra of the cells.

Table 1
Comparison of the photovoltaic properties of DSSCs with Graphene/FeS_2 and Pt counter electrodes.

Sample	FF (%)	Efficiency (η%)	Voc (V)	Jsc (mA/cm^2)
FeS_2 CE	56	7.43	0.78	17.01
Pt CE	54	6.40	0.76	15.60

DSSC under AM 1.5G 1-Sun illumination (100 mW/cm^2,) shows 7.43% sun light into electricity conversion efficiency (η) which is 16.1% higher than that of Pt CE based DSSC (η_{PtCE}=6.45%). The performance of devices with Pt and Graphene/FeS_2 CEs is summarized in Table 1. The improvement of photo conversion efficiency (PCE) mainly results from the increase of J_{SC}. The increase of J_{SC} can be attributed to rapid interconversion between I_3^- and I^- and absorption of more photons by the FeS_2 structures on the CE side. We showed that graphene/FeS_2 CE provide large effective surface area owing to their rough morphology, thus leading to low charge transfer resistance. EQE is shifted upward in DSSCs when graphene/FeS_2 instead of conventional Pt was used as the counter electrode. EQE spectra shows typical characteristics of the N719 dye at 530 nm wavelength in Fig. 3(d). The increased shift of the EQE curve is an indication that extra electrons are generated in the devices. The shift is consistent with the increase in the value of Jsc, apparently seen in Fig. 3(c). For similar dye loading conditions, this increased photocurrent could be due to the light reflection from the counter electrode. It has been clearly shown that graphene/iron pyrite (FeS_2) thin films have a good catalytic activity and it is an ideal counter electrode for DSSC applications.

4. Conclusion

In conclusion, we have demonstrated a novel counter electrode with graphene/iron pyrite (FeS_2) thin films in DSSC. It has been shown that graphene/pyrite thin films exhibits higher surface area and good catalytic activity compared to the conventional Pt counter electrode. Higher solar conversion efficiency of 7.43% compared to 6.4% of the Pt based DSSC is obtained by using graphene/FeS_2 as CE. This corresponds to 16.1% efficiency improvement through the usage of earth abundant materials as an alternative for Pt. According to the results gathered from the study, this research not only provides a promising approach to enhance the performance of DSSCs and also reduce the cost by using earth abundant and catalytically more active graphene/iron pyrite thin films.

Acknowledgments

This project was supported by Türkiye Bilimsel ve Teknolojik Arastirma Kurumu (Scientific and Technological Research Council of Turkey) (TUBITAK) Project number: 114F292. The authors would like to thank TUBITAK for giving a support.

References

[1] M. Gratzel, Dye-sensitized solar cell, J. Photochem. Photobiol. C 4 (2003) 145–153.
[2] P. Poudel, Q. Qiao, Carbon nanostructure counter electrodes for low cost and stable dye-sensitized solar cells, Nano Energy 4 (2014) 157–175.
[3] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-sensitized solar cell, Chem. Rev. 110 (2010) 6595–6663.
[4] S. Shukla, et al., Iron pyrite thin film counter electrodes for dye-sensitized solar cells: high efficiency for iodine and cobalt redox electrolyte cells, ACS Nano 8 (2014) 10597–10605.
[5] F. Ghamouss, et al., Characterization of screen printed carbon counter electrodes for Co(II)/(III) mediated photoelectrochemical cells, Electrochim. Acta 55 (2010) 6517–6522.
[6] Q. Xuefeng, X. Yi, Q. Yitai, Solventothermal synthesis and morphological control of nanocrystalline FeS_2, Mater. Lett. 48 (2001) 109–111.
[7] A. Ennaoui, et al., Iron disulfide for solar energy conversion, Sol. Energy Mater. Sol. Cells 29 (1993) 289–370.
[8] B. Kılıç, H. Telli, S. Tüzemen, A. Başaran, G. Pirge, Design of hybrid nanoheterostructure systems for enhanced quantum and solar conversion efficiencies in dye-sensitized solar cells, J. App Phy 1–10 (2015), JR14-11554R1.