RESEARCH PAPER

New High-Efficiency Protective Coating Containing Glycidyl-POSS Nanocage for Improvement of Solar Cell Electrical Parameters

Kamal Ghani*, Narges Kiomarsipour, Mahdi Ranjbar

Department of Chemistry, Malek Ashtar University of Technology, Shahin-shahr, Iran

ARTICLE INFO

ABSTRACT

Article History: Received 22 October 2018 Accepted 06 December 2018 Published 01 January 2019

Keywords: Antireflection Poss Solar Cell Transmittance

Various antireflection thin films are often used to cover glass to increase solar cell electrical parameters. In the recent years many efforts have been done to develop and improve of solar cell films with high electrical output. One of the most important challenges of obtaining of high-efficiency thin films of solar cells is creation an effective light trapping system. The new polymeric protecting materials are called polyhedral oligomeric silsesquioxanes (POSS) that can improve the solar cells properties. In the present work, firstly Tetraglycidyloxypropyl tetramethyl POSS was synthesized via sol-gel method and used to prepare TGTM POSS-silica nanocomposite, then it was applied on solar cell slides. The structural, morphological, thermal, optical and electrical properties were investigated by TEM, FTIR, NMR, FE-SEM, TGA, UV-VIS spectroscopy and solar simulator. Evaluation of the obtained results showed that the efficiency of solar cells was improved twice or more (50%) compared with that without POSS coating. The coatings transmittances were equal 100% that are ideal for solar cell films. The solar cells stability to solar light with POSS coating was also evaluated. The obtained results showed that the degradation of solar cell transmission.

How to cite this article

Ghani K, Kiomarsipour N, Ranjbar M. New High-Efficiency Protective Coating Containing Glycidyl-POSS Nanocage for Improvement of Solar Cell Electrical Parameters. J Nanostruct, 2019; 9(1): 103-111. DOI: 10.22052/JNS.2019.01.011

INTRODUCTION

Low refractive index thin surface coatings have been applied as antireflective (AR) coatings for optical applications such as display devices, solar cells and optical lenses. The materials used in the manufacture of an effective solar cell are chosen to give the maximum electrical output for a given radiation input and are usually a poor optical match to the incident medium; that cause to reflect of the significant fraction of the incident radiation by the cell and finally cause to loss of efficiency. In effective cells the reflectance must be reduced to a lower value, either by application of an advanced antireflection coating or by producing an outer surface which entraps light and leads to multiple scattering of the incident radiation [1].

Whereas most semiconductors have high refraction indices consequently they have high reflectance; finally a large amount of incident light is lost by reflection at the surface of the solar cell. An effective antireflection coating can lead to a very large increasing in the transmittance to the cell. Generally, dielectric antireflection coatings significantly reduce the reflectance in the spectral response SR (X) range of the cell, while also maintaining a suitable low reflectance in the IR portion of the spectrum [2]. Antireflection coatings have attracted much study interest because of their various potential applications for more effective sunlight collecting. An ideal antireflection coating should match the following conditions: the coating refractive index $n_{r_{i}}$ ($n_{i} \times n_{i}$)^{1/2}, where n_{i} and n_{i} are

* Corresponding Author Email: kghani@mut-es.ac.ir

This work is licensed under the Creative Commons Attribution 4.0 International License. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

the refractive indices of the air and substrate, respectively; the thickness of the coating should be $\lambda/4 \times n_c$, where λ is the wavelength of the incident light [3]. The refractive index of the coating can be lowered still by importing porosity to it. Various porous silica materials are recently promising candidate due to their adjustable refractive index, high durability, and environmental resistance [4-8]. POSS nanocage additive, similar to these porous silica materials, can trap light in its hollows and reducing refractive index consequently increasing the efficiency.

In additional the required optical properties, solar cell coatings must be resistant to ultraviolet radiation. A new class of advanced materials has recently been discovered during the studying and investigation for improvements in optical plastics. These new polymeric protecting materials are called "polyhedral oligomeric silsequioxanes". The technology is exclusively manufactured by Hybrid Plastics Inc. (Hattiesburg, MS) under the acronym POSS[®] nanocomposites. These new materials have improved significantly the solar cells technology. POSS nanoprotectings can be incorporated into all known resins using common polymerization or compounding techniques to afford customized, optically transparent materials with entirely new performance levels [9].

Polyhedral oligosilsesquioxane (POSS) is one of many types of silsesquioxane molecules. The term silsesquioxane refers to the molecules, whose chemical structure follows the basic composition of RnSinO_{1.5}n, for example Me₈Si₈O₁₂. Here, the

R-group, also called the vertex group for polyhedral molecules, may be alkyl, hydrogen, aryl arylene, alkylene, among others. Such silsesquioxanes can shape oligomeric organosilsesquioxanes ($CH_3SiO_{1.5}$) n through chemical reactions and the chemical structures of the derivative silsesquioxanes are completely versatile. The molecular arrangement of silsesquioxanes can be sorted into two classes: (a) noncaged structure and (b) caged structure, as indicated in Fig. 1 (a,b). As shown in Fig. 1 (a), the non-caged silsesquioxane molecules can be more classified into: (a) random structure; (b) ladder structure, and (c) partial-cage structure [10].

In the present work, firstly POSS nanocage of Tetraglycidyloxypropyl tetramethyl POSS under the acronym TGTM POSS was synthesized, characterized and used in silicate binder. Then the electrical parameters of prepared solar cells was evaluated. Incorporation of TGTM POSS in silicate binder and its application as an advanced solar cell cover for improving the solar cell electrical parameters was evaluated for the first time.

MATERIALS AND METHODS

Preparation of TGTM POSS

The used synthesis method for preparation of TGTM POSS is similar to reported procedure by Innocenzi et.al [11]. 3-Glycidoxypropyltrimethoxysilane (GPTMS 96% Aldrich) was used as the organically modified alkoxide, methyltetraethylorthosilicat (MTEOS), sodium hydroxide NaOH, (Aldrich 98%) as the basic catalyst and distilled water for hydrolytic reactions; all the



Fig. 1. Chemical structures of silsesquioxanes. (a) non-caged silsesquioxanes: (i) random, (ii) ladder; (iii) partial caged structures, and (b) caged silsesquioxanes: (i) T_s, (ii) T₁₂ structures [10].

J Nanostruct 9(1): 103-111, Winter 2019

reagents were used as received without further purification. The molar ratio of the components was GPTMS:H₂O:NaOH:MTEOS=0.5:0.5:0.5:0.167; in a typical preparation, GPTMS and MTEOS in the same molar ratios were stirred for 10 minutes. Distilled water and NaOH were stirred together separately. GPTMS and MTEOS solution was added dropwise to the NaOH aqueous solution under severe stirring at 25°C; the obtained clear sol became transparent in a few minutes after the addition of GPTMS.

Preparation of GPTMS/TEOS sols

In two containers were poured 40 ml absolute ethanol. To one of them was added 6.24 g TEOS and then added 16.8 g GPTMS under stirring at room temperature. Into another container 1.8 g H2O and 2.4 g hydrochloric acid were added and stirred at room temperature for 20 minutes. This obtained solution was added to later solution and stirred, then it was refluxed for 4 h at 85°C. The produced viscose solution was used as binder.

Preparation of POSS protective coating

The POSS coating was prepared by adding 10 wt% POSS into GPTMS/TEOS sol [12]. For measuring dried weight, 2 mL of containing POSS sol was poured on a lam and put in oven. After drying completely, the dried weight of sol was assessed. Then 10 wt% of POSS nanocage as an additive was added to synthesized resin. After that, solution was refluxed for three hours at 70 °C. The second refluxing was conducted for three hours at 85 °C. The obtained viscose clear sol at the end was covered on slides. Before applying the solution onto solar cell substrates, all slides were washed completely by water and soap and then cleaned by acetone, alcohol and dichloromethane respectively. The used silicone solar cell slides are shown in Fig. 2 and their characteristic are shown in Table. 1. To make coatings with same thicknesses, the obtained viscose sol were hand spread on top of each slide at five mils in thickness. Some of the slides were pre-coated with TiO, by PVD method. The same procedure was used for slides with and without TiO, superficial layer. The POSS coated solar cells were cured in oven at 80 °C overnight. They were then more cured at 80 °C for four days. After complete curing, slides were put in special container for keeping away any contamination.

Characterization of POSS nanocage

Structural properties were detected by means of Fourier transform infrared spectroscopy (FTIR) (Tensor 27) made in Bruker co. Morphology of samples were investigated by Hitachi S-4160 Field Emission Scanning Electron Microscopy (FE-SEM) at an accelerating voltage of 15 Kv

 $\begin{tabular}{|c|c|c|c|} \hline Table 1. Characteristics of solar cell slides \\ \hline Cell Resistance & Microstructure & Type & Thickness & Size \\ \hline (ohm.cm) & (mm) & (mm) \\ \hline 0.2 - 0.4 & Polycrystal & P & 330\pm40 & 100*100 \\ \hline \end{tabular}$



Fig. 2. The used solar cell slides

and the Philips CM10 Transmission Electron Microscope (TEM), using an accelerating voltage of 200 kV. The diffuse reflectance spectra of coated solar cells were measured by JASCO V-670 UV-Vis Spectrophotometer (in the range of 220-2200 nm). Electrical parameters were measured by Sharif University Solar Simulator. 29Si NMR measurements were performed on a DSX spectrometer (Bruker). Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q50 thermogravimetric analyzer. Measurements were performed under air atmosphere. 10 mg of the sample was heated from 100 to 600 °C at a heating rate of 10 °C/min.

RESULTS AND DISCUSSIONS

Fourier Transform Infrared Spectroscopy (FTIR) has been used to investigate of many silsesquioxane structures. The FTIR spectrum of as-synthesized POSS was shown in Fig. 3. Characteristic vibration

present in the IR spectrum of silsesquioxane is the Si–O–Si asymmetric stretching, at 1100–1140 cm⁻¹ or at 1057–1085 cm⁻¹ in case of strained geometry. As seen in this figure, a strong absorption Si-O-Si symmetric stretching peak observed at ~1100 cm⁻¹ that is a general feature of POSS derivatives and confirmed that the POSS cage-type structure is formed [13-15]. The C–O–C stretching vibration of cycloaliphatic epoxide ring is appeared at ~750 cm⁻¹ [16].

The obtained ²⁹Si NMR spectrum was shown in Fig. 4 and indicated that the mixture is made mainly of octameric fully condensed T_3 species. There are many possible isomers, so many discrete signals collapsed together in one broad peak at -66.380 ppm [12]. These data suggested the formation of some types of cyclic or even ladder like structures. The signals at -66.380, -67.016, -67.946, -68.167 ppm are referred to T_3 units in cubic T_8 cage structures. T_7 signals at -58.858 and -59.072 are an



indication that a great part of the T_8 cages are not fully condensed, with one of the bonds between silicon atoms not formed, leaving an open cage. This is in agreement with the reaction conditions that are expected at very so high pH; cyclization of organically modified alkoxides is a well-known phenomenon that can be observed in highly acidic or basic conditions [11]. The peaks at 42.869 ppm and 51.553 ppm, respectively, related to the epoxide ring of glycidyl POSS. The abroad areas under the T_2 and T_3 peaks proved that the almost all of POSS is nanocage [17,18]. Fig. 5 illustrates the suggested mechanism for the interactions between silica and oligosilsesquioxane POSS [19].

Selected thermal gravimetric trace (TGA) was shown in Fig. 6. For all of the hybrid systems a similar two-stage decomposition process was observed. The first drop on the TGA curve is related





-

J Nanostruct 9(1): 103-111, Winter 2019

to water dehydration (~ 350 °C), while the second mass loss, analogously as in the case of hybrids made from support precipitated from aqueous solutions, is related to the degradation of organic groups present in the corners of the POSS cage. The process continued up to total degradation of the organic groups substituted at the silicon atoms of the POSS skeleton [19]. For glycidyl POSS the onset temperature of mass loss is 350 °C and the residual masses are 55% [17]. In the heating stage, POSS molecules transformed into the SiO₂ particles via the condensation reaction among Si–O–Si at high temperatures.

The FE-SEM micrographs of as-synthesized POSS was shown in Fig. 7 (a-d). As seen in Fig. 7 (a,b), POSS has accumulated morphology with particle size distribution in the range of 15-25 nm. The FE-SEM micrographs of POSS prepared coating and its cross-section were shown in Fig. 7 (c,d). From this figure can be seen that the surface of prepared coating was completely smooth and the thickness of coating was nearly 30 µm.

The products were further characterized by TEM, shown in Fig. 8. As shown in Fig. 8 (a,b), all of the prepared sample on the TEM grids showed nano-sized powder, which confirm the SEM results.



Fig. 7. The FE-SEM micrograph of: (a,b) as-synthesized POSS nanocage additive, (c) the prepared coating with POSS additive, (d) the cross-section micrograph of prepared coating.

J Nanostruct 9(1): 103-111, Winter 2019

K. Ghani et al. / Glycidyl-POSS Nanocage for Improvement of Solar Cell



Fig. 8. The TEM micrographs of: (a,b) as-synthesized POSS nanocage additive.



Fig. 9. The I–V curves of a solar cell with and without POSS coating before and after UV radiation

The I-V curves for solar cells before and after application of the POSS coating are shown in Fig. 9. It can be seen that the short circuit current increased from 30.60 A to 40.43 A and the efficiency improved from 4.69% to 7.23% due to the presence of the POSS film. The ratio of the conversation efficiency before and after applying the POSS coating was used to determine the improvement percent due to the applied coating. The cell conversation efficiency increased from 4.69 to 7.23 percent. Table 2 provides a listing of cell performance data of the pre- and post-POSS coatings. As seen in this table, the efficiency of coated POSS solar cells was improved more two time than that of without POSS coating. The POSS

J Nanostruct 9(1): 103-111, Winter 2019

nanoporous morphology can effectively reduce the refractive index of the film, thus antireflectivity can be obtained with a suitable film thickness. In coatings containing POSS the assembly of nanoparticles introduced nanopores in the coating contributes to the decrease of the effective refractive index of the film and traps the incident light. Therefore, the achieved results from I-V measurements confirm that the nanopores play a vital role in the reducing of the refractive index of the film. The ability of reducing reflectivity from cells is especially desirable for the solar cells since the sunlight does not always irradiate the solar cell vertically. The decreasing transmittance at higher sunlight incidence angles will inevitably result in K. Ghani et al. / Glycidyl-POSS Nanocage for Improvement of Solar Cell

Sample Number	Description of the sample	Open circuit voltage (V _{oc}) (V)	Short circuit current (I _{sc}) (A)	Fill factor (FF)	Efficiency (Eff) (%)
1	Without POSS coating	0.56	30.60	0.27	4.69
	With POSS coating	0.55	40.43	0.32	7.23
2	Without POSS coating	0.56	27.90	0.26	4.09
	With POSS coating	0.55	41.79	0.30	6.97
3	Without POSS coating	0.53	24.40	0.28	3.68
	With POSS coating	0.55	34.73	0.28	5.44
4	Without POSS coating	0.56	27.20	0.28	4.32
	With DOSS conting	0.55	41.22	0.20	671

Table 2. Electrical parameters of the solar cells without and with POSS coatings



Fig. 10. The transmittance spectra of coated solar cells with POSS coatings before and after UV irradiation

a sharp decrease in the power output of solar cells. With the advanced antireflective coating on the solar cell, more output power and the cells efficiency, especially at higher incident angles, can be expected. The output increase is due to the less sunlight reflection from the coating, thus more sunlight is received by the cell and is transformed into electricity [3]. For evaluation of light stability of POSS protective coating, solar cells with and without POSS coating were exposure to UV radiation. Exposure of coatings to natural environment often results in the loss of transmittance due to defects generated from environment. The I-V curves of solar cell with and without POSS coating and after UV radiation were indicated in Fig. 9. As seen in this figure, changes of conversation efficiency of cell was so negligible. The efficiency after UV irradiation was same that before irradiation and approved that the new advanced coatings can protect the solar cells from sun light destructive ultra violet. This result confirms the possibility of using POSS additive as a protective antireflecting coating for silicon solar cells. The transmittance spectra of coated solar cells with POSS coatings before and after UV irradiation are indicated in Fig 10. It can be seen in this figure that the coatings had highly transparency in the visible light spectrum that allowing to maximum power generation by the solar cells and the changes in transmittance caused by UV radiation were no significant.

CONCLUSION

The present paper reported the striking effect of a novel POSS additive that was used in silicate resin as protective coating on solar cells. Our reported findings in this paper were based on obtained data from TEM, FE-SEM micrographs as well as FT-IR, NMR, TGA and UV/VIS absorption spectroscpy of the samples. In the current work, POSS nanocage was synthesized and added into silicate binder as additive. The obtained results indicated that solar cell efficiency improved almost 50% compared with that of the initial state (without POSS coating). The POSS nanoporous morphology can effectively reduce the refractive index of the film, thus antireflectivity can be obtained with a suitable film thickness. Evaluation of stability to sun light simulated UV also indicated that degradation of optical properties, for example transmission, was negligible and this additive not only improved the efficiency but also protected the solar cells to sun light damages.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

REFERENCES

- 1. Gandham B, Hill R, Macleod HA, Bowden M. Antireflection coatings on solar cells. Solar Cells. 1979;1(1):3-22.
- Demichelis F, Minetti-Mezzetti E, Perotto V. Optical studies of multilayer dielectric-metal-dielectric coatings as applied to solar cells. Solar Cells. 1982;6(4):323-33.
- Lu X, Wang Z, Yang X, Xu X, Zhang L, Zhao N, et al. Antifogging and antireflective silica film and its application on solar modules. Surface and Coatings Technology. 2011;206(6):1490-4.
- Shimizu W, Murakami Y. Microporous Silica Thin Films with Low Refractive Indices and High Young's Modulus. ACS Applied Materials & Interfaces. 2010;2(11):3128-33.
- Zhang J, Lan P, Li J, Xu H, Wang Q, Zhang X, et al. Sol–gel derived near-UV and visible antireflection coatings from hybridized hollow silica nanospheres. Journal of Sol-Gel Science and Technology. 2014;71(2):267-75.
- Zhang X, Lan P, Lu Y, Li J, Xu H, Zhang J, et al. Multifunctional Antireflection Coatings Based on Novel Hollow Silica–Silica Nanocomposites. ACS Applied Materials & Interfaces. 2014;6(3):1415-23.
- Liu B-T, Yeh W-D. Antireflective surface fabricated from colloidal silica nanoparticles. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2010;356(1-3):145-9.
- Du X, He J. Facile Fabrication of Hollow Mesoporous Silica Nanospheres for Superhydrophilic and Visible/Near-IR Antireflection Coatings. Chemistry - A European Journal. 2011;17(29):8165-74.
- 9. Brandhorst H, Isaacs-Smith T, Wells B, Lichtenhan J, Fu

B. Poss[®] Coatings as Replacements for Solar Cell Cover Glasses. 4th International Energy Conversion Engineering Conference and Exhibit (IECEC); 2006/06/26: American Institute of Aeronautics and Astronautics; 2006.

- Wu J, Mather PT. POSS Polymers: Physical Properties and Biomaterials Applications. Polymer Reviews. 2009;49(1):25-63.
- 11.InnocenziP, Figus C, Kidchob T, Valentini M, Alonso B, Takahashi M. Sol-gel reactions of 3-glycidoxypropyltrimethoxysilane in a highly basic aqueous solution. Dalton Transactions. 2009(42):9146.
- Jerman I, Šurca Vuk A, Koželj M, Švegl F, Orel B. Influence of amino functionalised POSS additive on the corrosion properties of (3-glycidoxypropyl)trimethoxysilane coatings on AA 2024 alloy. Progress in Organic Coatings. 2011;72(3):334-42.
- Pescarmona PP, Maschmeyer T. ChemInform Abstract: Oligomeric Silsesquioxanes: Synthesis, Characterization and Selected Applications. ChemInform. 2010;33(29):nono.
- Peng D, Qin W, Wu X. A study on resistance to ultraviolet radiation of POSS–TiO2/epoxy nanocomposites. Acta Astronautica. 2015;111:84-8.
- Wu Y-C, Kuo S-W. Synthesis and characterization of polyhedral oligomeric silsesquioxane (POSS) with multifunctional benzoxazine groups through click chemistry. Polymer. 2010;51(17):3948-55.
- Ramírez C, Rico M, Torres A, Barral L, López J, Montero B. Epoxy/POSS organic–inorganic hybrids: ATR-FTIR and DSC studies. European Polymer Journal. 2008;44(10):3035-45.
- Rahman MM, Filiz V, Khan MM, Gacal BN, Abetz V. Functionalization of POSS nanoparticles and fabrication of block copolymer nanocomposite membranes for CO2 separation. Reactive and Functional Polymers. 2015;86:125-33.
- Wu K, Song L, Hu Y, Lu H, Kandola BK, Kandare E. Synthesis and characterization of a functional polyhedral oligomeric silsesquioxane and its flame retardancy in epoxy resin. Progress in Organic Coatings. 2009;65(4):490-7.
- Szwarc-Rzepka K, Marciniec B, Jesionowski T. Immobilization of multifunctional silsesquioxane cage on precipitated silica supports. Adsorption. 2013;19(2-4):483-94.