2011

Design, Preparation and Characterization of Polystyrene Nanospheres Based-Porous Structure towards UV-Vis and Infrared Light Absorption

Pratama Jujur Wibawa, *Universiti Tun Hussein Onn Malaysia*
Mohd Arif Agam, *Universiti Tun Hussein Onn Malaysia*
Hashim Saim, *Universiti Tun Hussein Onn Malaysia*
Hadi Nur, *University Technology Malaysia*

2011 International Conference on Physics Science and Technology (ICPST 2011)

Design, Preparation and Characterization of Polystyrene Nanospheres Based-Porous Structure towards UV-Vis and Infrared Light Absorption

Pratama Jujur Wibawa[a,b*], Hashim Saim[c], Mohd. Arif Agam[c] and Hadi Nur[d]

[a]Microelectronic and Nanotechnology-Shamsuddin Research Center (MiNT-SRC), Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia
[b]Department of Chemistry, Faculty of Sciences and Informatics (formerly Faculty of Mathematics and Natural Sciences), Diponegoro University, Jl. Prof. H. Soedarto, S.H. No.1 Tembalang, Semarang, Indonesia,
[c]Department of Physics, Faculty of Sciences, Technology and Human Development,Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia
[d]Ibnu Sina Institute for Fundamental Science Studies,Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

Abstract

Porous Polystyrene nanospheres (PSNs)-Cd metal thin film of about 375.72 angstrom (Å) on hydrophilic silicon wafer has been successfully fabricated from its liquid colloidal prepared by 40 KHz ultrasound for 45 minute at room temperature. This porous fabrication was aiming to confirm the proposed structure of PSNs based-porous thin film models depicted in Fig.1. Surface morphology of the porous thin film explored with a field emission scanning electron microscopy (FESEM) showed that Cd metals atomic particles might be deposited on the PSNs particles surface so that they could enhance the porosity of the thin film material. Absorption capability of the porous thin film assayed using both ultraviolet-visible (UV-Vis) and infrared (IR) light proved that Cd metals atomic particles were a main part of the porous thin film which could enhance significantly the absorption performance. It could be concluded that both kind of nano- sunken and nano-wells unique binding sites might have been generated inside the pores during fabricating them.

1. Introduction

Porous structure is the most important features of any material that receiving great attention since the ancient era due to its adsorption and diffusion capability. The physical properties of pores or pore channels of porous material was determined by pore shape, pore size and pore structure [1] and maybe

*Corresponding author: Tel.: +60-13-7657849, fax: +62-24-76489077
E-mail address: pratamajw@gmail.com. and pratama_jw@undip.ac.id.

pore orientation or pore direction. Those all will affect on activity, selectivity and life time of the catalysis of the porous materials [1]. It is therefore very important to select, adjust and design properly the pore system of the material for getting the intended properties and functions. Recently, many synthetic porous materials made from organic polymer had been fabricated such as metal-organic nanocomposite [2], styrene-divinylbenzene (DVB) copolymers [3], oxide modified Zeolite composite and polymer-CNT composite [1]. This porous materials have got great attention due to their capability of adsorbent material for many various application of industrial processes such as catalyst [1,4], chemicals sensor [5,2] and drug delivery [6], waste water treatment [7], membrane fuel cell [8-10], fuel cell electrode [11] and soon.

In addition, polystyrene especially polystyrene nanospheres (PSNs)-based porous materials have many advantages compared to the others due to it was not only very simple but also any functional group was not exist in the molecule so that any metals ions or atoms can be incorporated easily through its aromatic rings *pi* electrons interaction only. In case of porous materials generated by PSNs particularly of 200 nm size we would like to divide it into two kinds of pore terms, the first one is intra or inside-PSNs pores revealed among polystyrenes chains constructed the PSNs particles bodies and the second one is inter-PSNs pores revealed among the PSNs particles bodies. In the first term, four valuable models of the pores structure which generated by disorder multiple folding and bending of the polystyrenes chains constructed the PSNs particles bodies were proposed. Those are (1) India traditional trumpet-like model, (2) face-to-face junction bottle neck-like model, (3) randomly irregular form model, and (4) straightforward pipe-like model, and all of them were depicted in Fig. 1(A,a), (A,b), (A,c) and (A,d) respectively. In this context, each PSNs particle body was possible to have all of the four pores models together such as illustrated in Fig.1(A,e) but at least one of the four models pores exist inside the PSNs particle bodies.
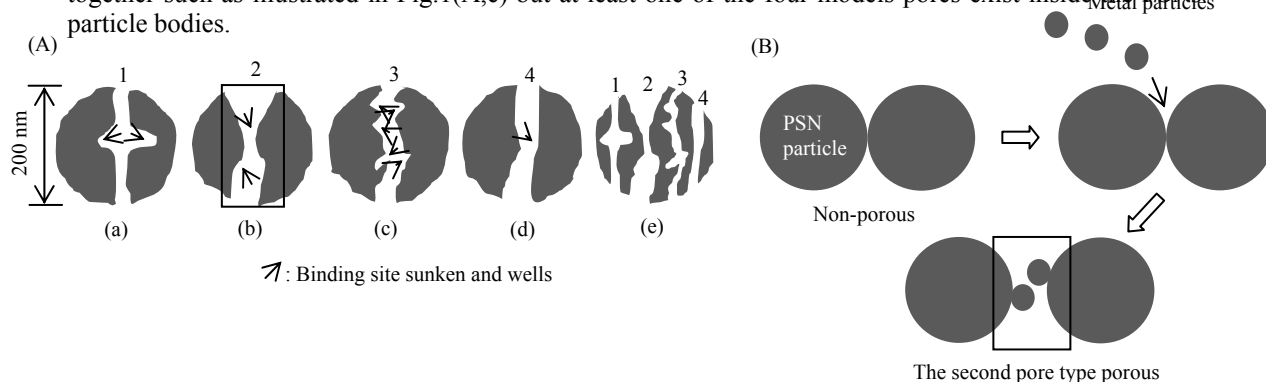
Figure 1. The proposed model of pores structure generated inside/intra-PSNs particle body of 200 nm sizes (A), the pore structure model generated by metal atomic particles inter-PSNs particles bodies (B).

In these models we assumed that the pores were generated from disorder multiple folding and bending of the polystyrene chain backbone constructed the PSNs particles bodies. This folding and bending would subsequently form many specific sunken and wells-like shapes in nano size namely nano-sunken and nano-well to bind any absorbed matter. Thus, a pore that possess more sunken and wells would also possess more effective binding site for the adsorption process. Therefore, the highest capacity and capability of absorption will be taken place on a pore model of Fig.1(A,c) due to five binding sites exist therein. In contrary, the lowest that will be taken place on a pore model of Fig.1 (A,d) due to it has just one binding site.

Moreover, pores generated from inter-PSNs particles bodies such as depicted in Fig.1(B) would be revealed when metal atomic particles well deposited between two PSNs particles bodies. The structure of the pores would be similar to face-to-face junction bottle neck-like model which appeared inside-the PSNs particles. It would be very clear understood that the pore size will become significantly increased as

metals particles were deposited among the PSNs particles bodies because of they can push the PSNs bodies to little bit move away each other.

Considering the both kinds of models it could be predicted that any thin film material fabricated from PSNs particles will have many advantages and have interesting unique properties particularly when it was used as an adsorbent/absorbent and chemical catalyst. In this context, many researchers already used non-spherical polystyrene to fabricate polystyrene-metal-based porous materials [12,13-16] using metals nanoparticles generated *in-situ* from its according metal salts precursors such as Cd from $CdCl_2$ [16], from $Cd(CH_3CO_2)_2$ [17] and from $Cd(NO_3)_2$ [18]. However non-spherical polystyrenes of course did not have many pores revealed inter spherical particles bodies but just from inter their chains backbone only. As a result, capacity and capability of adsorption/absorption would be low compared to that of PSNs made from. Therefore this paper explained the unique characters of prepared polystyrene nanospheres-metal-based porous thin film for UV-vis and IR light absorption.

1. Experimental Section

Firstly we properly prepared colloidal PSNs-Cd metal particles by the following procedure, 1% w/v, 5 µl Cadmium nitrate-4-hydrate salt (Cd $(NO_3)_2.4H_2O$, Mr = 308.48 gram/mol) of 98 % grade (Cica Reagent-Kanto Chemical Japan) was properly dispersed into 5 µl PSNs (200 nm size, 1 % w/v) and subsequently added with deionised (DI) water up to 100 µl total volume. This dispersion system was then homogenized by vigorously shaking and irradiated with 40 kHz ultrasonic for 45 minutes (Ultrasonic Cleaner Power sonic 405; made in Korea). Secondly porous PSNs-Cd metal thin film was fabricated on a hydrophilic 1 x 1 cm^2 silicon (Si) wafer (100 single crystal orientation, p-doped, resistivity of 1.0-20.0 ohm.cm and thickness of 475-575 µm) by the following procedure, the 1 x 1 cm^2 Si wafer was warmed at 80^oC in modified piranha solution made from saturated HCl/H_2O_2 = 3:1 for about 20 minutes to remove any oily matter then it was rinsed up with DI water and dried under atmospheric air flow of a laboratory room. After that, 10 µL of the PSNs-Cd metal colloid that have already prepared was gently dropped onto the hydrophilic Si wafer. Let it in a position of about 5° slope at 20^oC room temperature for the intended thin film through self-assembly process. By the same procedure, pristine 200 nm PSNs of 0.1%w/v thin film was also fabricated on the same Si wafer for a reference thing.

Furthermore, porosity of them was confirmed by exploring its surface morphology employing a Field emission scanning electron microscope (FE-SEM JEOL JSM-7600F, Made in Japan). The samples were carefully loaded on a specific FESEM sample holder then introduced it into the FESEM chamber setup on vacuum of about $10x10^{-5}$ Pa. The surface morphology images was then scanned with electron beam of about 2.00 kV, LEI SEM detector mode and scanning wide distance (WD) of about 9.6-9.8 mm. The optimum magnifications scanning of about 10,000 to 50,000 were preferential mode for the best images. Image magnification was defined as the ratio of the length of the scan on the Cathode Ray Tube (LCRT) and that of the scan on the sample specimen (LSpec).

Moreover, the both kind of thin film materials were independently irradiated with both ultraviolet – visible (UV-Vis) and infrared (IR) lights to characterize its absorption capability performance towards electromagnetic waves. In this context, IR light beam was generated from a Fourier Transform Infra Red Spectrometer (Perkin Elmer FTIR Spectrometer LR 64912C, N3896 equipped with a universal Attenuated Total Reflectance (ATR) sample stage and a spectrum express FTIR software V1.3.2 Perkin Elmer LX100877-1, made by U.S.A). The sample was introduce properly on the ATR-FTIR sample stage and scanned on interpolated peak threshold of 0.5 %T, centre of gravity threshold of 0.0022 Absorbance (A), 10.0000 Absorbance Unit (A.U) and centre of gravity peak height of 0.2. Resulted spectra were then processed further with a series of action of data tune-up, ATR correction and finally normalization for the best accurate spectra. The smaller the number threshold, the less intensive are the peaks that may be detected. In addition, centre of gravity peak height 0.2 was the fraction of the peak to be used to calculate its centre gravity of peaks position.

On the other hand, UV-Vis light beam was generated from a F20 Thin Film Analyzer (Filmetrics Model 205-0135, Made in USA) equipped with FILmeasure software version 4.3.6. This instrument was

firstly calibrated by a Si reference wafer disc and SiO$_2$ on Si test wafer disc of 7272.0 Å thicknesses (Å stands for angstrom) then the sample was measured under this reference. At least three different area of about 0.5 cm in diameter of every sample was scanned five times using UV-Vis light beam of 300 nm up to 1100 nm wavelength generated from the instrument. The already installed FILmeasure software version 4.3.6 would then displayed a specific spectrum which correlated reflectance intensity versus UV-Vis wavelength and thoroughly converted the reflectance intensity become thickness of the according scanned area thin film layer in angstrom scale. The recorded thickness can be read exactly through a monitor.

2. Result and Discussion

2.1. Surface morphology clarification and electromagnetic waves absorption analysis

FESEM images of the PSNs-Cd metals thin film surface depicted in Fig.1(a), (a') and (a") showed clearly a nice porous-like structure material which might Cd metals lumps of about 44.5 nm deposited and then tighty attached on any PSNs particles surface.This porous structure was likely quite different from that of pristine PSNs Fig. 1(b). It was also shown that the size of PSNs have been reduced to about 176 nm due to ultrasonic irradiation of 40 kHz ultrasonic for 45 minutes during preparation of its colloidal . This similar shrinkage phenomenon was also reported by reference [19].
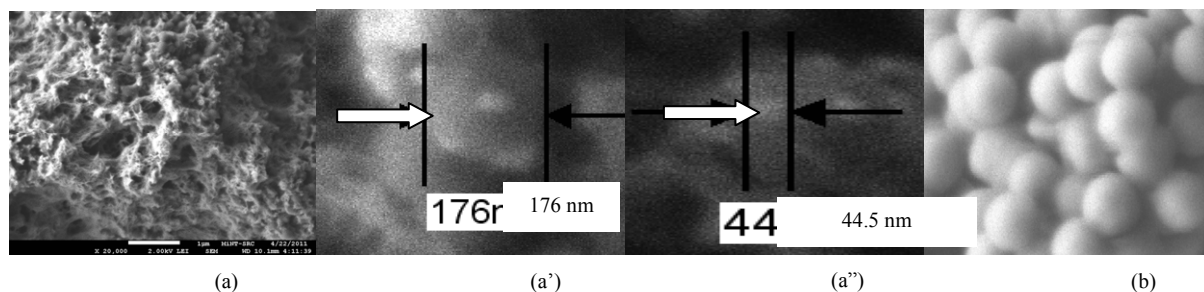
Figure 1. FESEM images of porous PSN-Cd metal thin film produced (a),(a'),(a") and that of pristine PSN (b)

On the other hand, the porous-like structure and the deposited Cd metals nanoparticles take responsible together for generating new optical properties of the materials especially in the interaction with both UV-Vis and IR lights. In the fact, porous PSNs-Cd thin film reflected UV-Vis light quite lesser (0.08 a.u – 0.14 a.u) than pristine PSNs (0.18 a.u – 0.23 a.u) for 500 nm to 1000 nm wave length range (a.u stands for arbittary unit) as shown in Fig.2. The similar phenomenon was also encountered in the infrared absorption, Fig.3 where the porous PSNs-Cd metal thin film absorbed infra red light more than the pristine PSNs since its base line transmittance intensity of the spectrum was lower (about 40 a.u up to 85 a.u range) than that of the pristine PSNs (about 90 a.u). These facts attributed that many unique pores in nano size were properly generated in the porous PSNs-Cd metal thin film as Cd metal atomic particles were incorporated either physically or chemically into among the PSNs particles. Detail discussion of UV-Vis and IR light absorption would be explained in section 2.2 and 2.3 respectively.
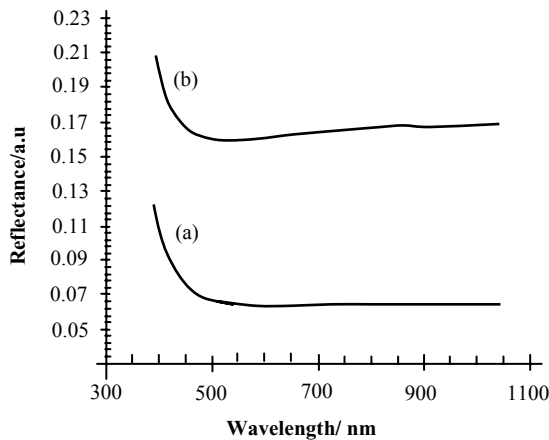
Figure 2. The UV-Vis reflectance spectrum of porous PSN-Cd metals thin film (a) and pristine PSN thin film (b)

Figure 3. The ATR-FTIR spectra of the porous PSNs-Cd metal thin film (a) and of pristine PSN (b) explored with Tune-Up, ATR correction and Normalization modes sequences. ph: phenyl (benzene ring residue of polystyrene)

2.2. **UV-vis light absorption analysis**

As we can see in Fig.2, UV-Vis reflectance spectra of porous PSNs-Cd thin film was lower than that of pristine PSNs thin film in throughout wave lenght range of 400 nm up to1000 nm. It attributed that absorption capacity of the first towards UV-Vis light was higher and better than that of the second one due to the existance of Cd metal particles. This case presenting that the Cd particles prefered creates nano-pores which have capability of electromagnetic waves absorption. It might photons of the lights had been absorbed properly rather by the nano-pores existed therein than by Cd metal atomic particles bodies. These nano-pores, of course, have unique nanostructure which make possible to bind the light photons on its specific binding site they have. It was suprise that this phenomenon matched to our proposed models of nano-pores structure such as depicted in Fig.1.

By these models we easier to undertand how the photons attached properly to the binding sites. In this moment we need to propose a new term of "nano-sunken" or "nano-well" which take very important role in the light photons absorption phenomena. We defined the new proposed term was a sunken or a well in nanoscale existing inside pores which generated during the according pores formation that having function for particularly light photons absorption. These "nano-sunken" or "nano-well" would have specific correlation to- and determine the absorption capacity of the materials. In this context, the much amount the "nano-sunken" or "nano-well", the higher the absorption capacity. Therefore, we possible to add the new term in one of nano-porous structure parameters for adsorption/absorption capacity value so that we have a new correlatian such as the following:

$$AC_n = f(A_p, A_{sw}, S_p, S_{sw}, Z_p, Z_{sw})$$

where AC_n, A_p, A_{sw}, F_p, F_{asw}, S_p, S_{sw} each is nano-absorption capacity of the material, the amount of nanopores, the amount of nanosunken or nanowell, the shape of nanopores, the shape of nanosunken or nanowell, the size of nanopores and the size of nanosunken or nanowell respectivelly.

In addition, we would like to concentrate our attention at 400 nm to 500 nm wave length range. We see that the light photons absorption of the both thin film materilas tends to increase as its reflectance decrease from 0.145 a.u to 0.09 a.u (porous PSN-Cd), and from 0.23 a.u to 0.18 a.u (pristine PSN). In contras, at 500 nm to 1000 nm wave length no significant change of the absorption could be observed
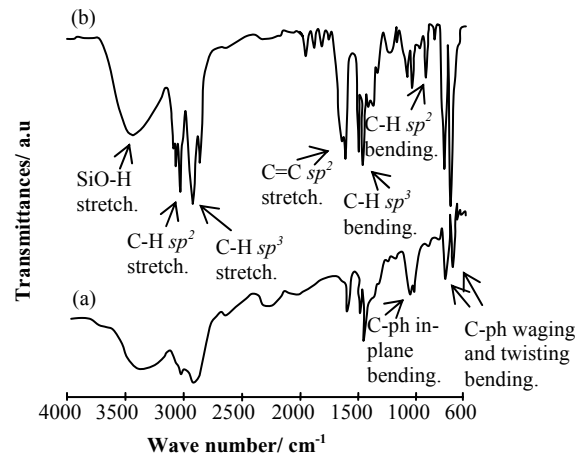
well from the porous PSN-Cd thin film, but indeed contrary, a litte bit change of that could bee seen from the pristine PSNs. In the first case, the UV-Vis reflectance intensity was kept at about 0.085 a.u, whereas in the second case that tends to litte bit inrease anymore from 0.18 a.u to 0.19 a.u.

2.3. **Infra red light absorption analysis**

It was shown in Fig.3 that porous PSNs-Cd metal thin film material absorbed infrared light more than pristine PSNs thin film since its base line transmittance intensity of the spectrum was lower (about 40 a.u up to 85 a.u range) than that of pristine PSN (about 90 a.u). In molecular level point of view, some specific bonds of polystyrene molecule mainly constructed the materials thin film also possessed transmittance intensity relatively higher than others. It could be interpreted properly that spectrum peak of 3365-3444 cm^{-1} represented hydrogen bond stretching vibration which be generated from the interaction of a silicon wafer SiO_2 support with phenyl hydrogen of the PSNs particles polystyrene chain. Spectrum peaks of 3029 cm^{-1} and 2927 cm^{-1} represented phenyl C-H stretching vibration of the polystyrene chain and H-C-H asymmetric stretching vibration of its chain backbone respectively. Spectrum peaks of 1603 cm^{-1} and 1493-1497 cm^{-1} and 1452-1456 cm^{-1} represented phenyl ring stretching vibration of its C=C-C "conjugative" system and either out of plane or in plane C-H bending vibration of its chain backbone respectively. Spectrum peaks of 1073 cm^{-1} and 1031 cm^{-1}) and 907-908 cm^{-1} represented phenyl in plane and out of plane C-H bending vibration respectively. The last, spectrum peaks of 755 and 699 cm^{-1} represented either phenyl ring wagging or twisting respectively [20-21].

Those mean, some bonds of polystyrene molecule constructed the porous PSNs-Cd thin film, i.e. SiO-H of SiO_2-phenyl ring, C-H of phenyl ring, and H-C-H of its chain backbone absorbed infrared wave relatively more than non porous pristine PSNs, whereas the other bonds, i.e. phenyl ring moiety, C=C-C "conjugative" system of phenyl ring, C-H of its chain backbone absorbed infra red wave relatively lesser than non porous pristine PSNs. The both would provide interesting impact to especially the structure of inside PSNs particles nonporous due to the bonds exist in the inside PSNs particles.

3. **Conclusion**

It was concluded that the prepared porous PSNs-Cd metal thin film material has unique porous structure which has ability to absorb both UV-Vis and Infrared light beam irradiated to it better than pristine PSNs particles one. The absorption capability of this material might because of the existence of nano-sunken and nano-wells binding site formed during fabrication. Absorption capacity of the pores could be enhanced significantly by depositing cadmium metal particles on PSNs particles surface so that it leads to generate pores structure similar to one kind of proposed pore model that have already designed, Fig.1(A,2).

References

[1]   Xie, Z.; Liu, Zh.; Wang, Y.; Yang, Q.; Xu, L. and Ding, W. An Overview of Recent Development in Composite Catalysts from Porous Materials for Various Reactions and Process, *International Journal of Molecular Science* 2010; **11:** 2152-2187.

[2]   Seo, J.S.; Whang, D.; Lee, H.; Jun, S.I.; Oh, J.; Jeon, Y.J. and Kim, K. A homochiral metal-organic porous material for enantioselective separation and catalysis, *Nature* 2000*;* **404**: 982-986.

[3]   Tsyurupa, M.P; Blinnikova, Z.K; Proskurina, N.A; Pastukhov, A.V; Pavlova, L.A. and Davankov, V.A. Hypercrosslinked Polystyrene: The First Nanoporous Polymeric Material, *Nanotechnology in Russia* 2009; **4(9-10)**: 665-675.

[4]   He, Ch. ;Li, J.; Cheng, J.; Li, L.; Li, P.; Hao, Z. and Xu, Z.P. Comparative Studies on Porous Material-Supported Pd Catalysis for Catalytic Oxidation of Benzene, Toluene, and Ethyl Acetat, *Ind. Eng. Chem. Res.* 2009; **48(15):** 6930-6936.

[5]   Dybtsev, D.M.; Chun, H.; Yoon, S.H.; Kim, D. and Kim, K. Microporous Manganese Formate: A Simple Metal-Organic Porous Material with High Framework Stability and Highly Selective Gas Sorption Properties, *J. Am. Chem. Soc.* 2004; **126(1):** 32-33.

[6]   Mume, E.; Lynch, D.E.; Uedono, A. and Smith, S.V. Investigating the binding properties of porous drug delivery systems using nuclear sensors (radiotracers) and positron annihilation lifetime spectroscopy-predicting conditions for optimum performance, *Dalton Trans.*2011; **40(23):** 6278-6288.

[7]   Hartman, M.; Kullmann, S. and Keller, H. Wastewater treatment with heterogeneous Fenton-type catalysts based on porous materials, *J.Mater. Chem.*2010; **20**: 9002-9017.

[8]   Gasda, M.D.; Eisman, G.A. and Gall, D. Nanorod PEM Fuel Cell Cathodes with Controlled Porosity, *Journal of the Electrochemical Society* 1010; **157(3):** B437-B440.

[9]   Tang, H.; Wang, S.; Pan, M. and Yuan, R. Porosity-graded micro-porous layers for plymer electrolyte membrane fuel cells, *Journal of Power Souce* 2007*; ,* **166**: 41-46

[10]   Gostick, J.T.; Fowler, M.W.; Ioannidis, M.A.; Pritzker, M.D.; Volfkovich, Y.M. and Sakars, A. Capillary pressure and hydrophilic porosity in gas diffusion layers for polymer electrolyte fuel cells, *Journal of Power Souces* 2005; Power-7121: 1-13, doi:10.1016/j.jpowsour.2005.05.086

[11]   Suffiner, J'; Kaserer, S.; Hahn, H.; Roth, Ch. and Ettingshausen. Sb-Doped SmO_2 Hollow Spheres Offering Micro- and Nanoporosity in Fuel Cell Electrode Structure, *Advanced Energy Materials* 2011*;* **1(4):** 4 pages.

[12]   Kamrupi, I.R; Phukon, P; Konwer, B.K. and Dolui, S.K. Synthesis of silver-polystyrene nanocomposite particles using water in supercritical carbon dioxide medium and its antimicrobial activity, *The Journal of Supercritical Fluids* 2011; **55**: 1089-1094.

[13]   Yoon, H; Lee, J; Park, D.W; Hong, C.K. and Shim, S.E. Preparation and electrorheological characteristic of CdS/Polystyrene composite particles, *Colloid Polym Sci*, 2010; **288:** 613-619.

[14]   Shi, D; Cho, H.S; Chen, Y; Xu, H; Gu, H; Lian, J; Wang, W; Liu, G; Huth, Ch; Wang, L; Ewing, R.C; Budko, S; Pauletti, G.M. and Dong, Z. Fluorescent polystyrene-Fe_3O_4 Composite Nanospheres for In Vivo Imaging and Hyperthermia, *Advanced Material* 2009; **21**: 2170-2173.

[15]   Antolini, F; Pentimalli, M; Luccio, T.Di; Terzi, R; Schioppa, M; Mirenghi, M.Re.L. and Tapfer, L. Structural characterization of CdS nanoparticles grown in polystyrene matrix by thermolytic synthesis, *Materials Letter* 2005*;* **59**:3181-3187.

[16]   Wu, D; Ge, X; Huang, Y; Zhang, Z. and Ye, Q. γ-Radiation synthesis of silver-polystyrene and cadmium sulfide-polystyrene nanocomposite microspheres, *Materials Letters* 2003; **57**:3549-3553.

[17]   Yoon, H; Lee, J; Park, D.W; Hong, C.K. and Shim, S.E. Preparation and electrorheological characteristic of CdS/Polystyrene composite particles, *Colloid Polym Sci*, 2010; **288:** 613-619.

[18]   Antolini, F; Pentimalli, M; Luccio, T.Di; Terzi, R; Schioppa, M; Mirenghi, M.Re.L. and Tapfer, L. Structural characterization of CdS nanoparticles grown in polystyrene matrix by thermolytic synthesis, *Materials Letters* 2005; **59**:3181-3187.

[19]   Zhang, Jianling. Liu, Dongxia. Yang, Guanying. Han, Buxing. Wu, Zhonghua. Effect of ultrasound on the microstructure of polystyrene in cyclohexane: a synchrotron small-angle X-ray scattering study, *Colloid Polym Sci,* 2007; **285:** 1275-1279.

[20]   Wibawa, Pratama Jujur; Agam, Mohd. Arif; Nur, Hadi; Saim, Hashim.   Changes in Physical Properties and Molecular Structure of Polystyrene Nanospheres Exposed with Solar Flux: 2010 International Conference On Enabling Science and Nanotechnology Escinano 2010. *AIP Conference Proceedings* 2011; **1341**: 54-61.

[21]   Luo, H. L. Sheng, J. and Wan, Y. Z. (2008). Preparation and characterization of TiO2/polystyrene core–shell nanospheres via microwave-assisted emulsion   polymerization, *Materials Letters* 2008*;***62**: 37– 40.