

Metals Particles-Covered Polystyrene Nanospheres: Facile Synthesis of Embedded Nanocatalyst

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

^{a,b,c} : University Tun Hussein Onn Malaysia ^d : University Technology Malaysia. arif@uthm.edu.my

Summary

Metals particles-covered Polystyrene Nanospheres (M-CPSNs) could be prepared through simple chemistry reaction. Analyzing Cd metal particles-covered PSNs as a model for metals particles-covered Polystyrene Nanospheres with ATR-FTIR spectrometry and FESEM, it prove that metals can be attached to polystyrene polymer. In determining the wave number ranges of 1700-1600 cm^{-1} and 1500-1200 cm^{-1} , significant different of ATR-FTIR spectra are generated between pristine PSNs and cadmium-covered PSNs. In addition, surface morphology of pristine PSNs thin film explored with FESEM revealed sharply different from that of cadmium-covered PSNs one. It indicated that PSNs particles surface have succesfully been fully covered by cadmium metals particles. Therefore it could be concluded that cadmium metals particles-covered PSNs thin film could be fabricated as a way to embedded metal to polymer which could be usefull in creating embeded nancatalysts and the model is illustrated as the following Fig. 2.

1. Introduction

Metal atomic particles-covered Polystyrene Nanospheres (M-CPSNs) could enhance basic properties of both materials, the substrate and metal particles, such as enhancing thermal and mechanical stability, electric and electronic conductance, optical and magnetic behaviour, hardness, and catalytic activity. M-CPSNs could be prepared through two strategies: First step through functionalizing the PSNs molecule framework with an active organic group and later followed by metals introduced onto the fuctionalized PSNs^{1,2}. The metal deposition or embedding of metals to the PSNs particles are common procedure to fabricate functionalized PSNs-based³⁻⁷ support material for biosensors⁸⁻¹⁰, ion exchange membranes¹¹⁻¹³, drug delivery agents¹⁴⁻¹⁷, acid-base catalytic materials¹⁸, manufacture of pattern nanostructure materials for light emmiting^{19,20}, specific adsorbant materials^{21,22}, metal-based catalytic materials^{23,24} and for intermediate material for fuel cell membrane and electrodes^{13,25}.

The determining factors of better dispersion in incorporating metals to functionalized PSNs depend to the chemical reducing agent which will prevent any undesirable alglomeration. Similar research of PSNs-based dispersion system without any additional chemical stabilizer has been reported elsewhere [26].

In this paper we reported the fabrication of cadmium (Cd) metal particles-covered PSNs prepared with common stabilizer addition of poly vinyl pyrrolidon (PVP) to study their physical interaction and chemical change through ATR-FTIR spectra as model of metal-covered PSNs material structure.

1. Results and Discussion:

Images of M-CPSNs in this case is Cd-CPSNs and the model of Cd-CPSNs structure was depicted in Fig 1 and Fig.2, respectively. The ATR-FTIR spectra of the Cd-CPSNs and bare PSNs explored under Tune-Up, ATR correction, Based

line correction and Normalization modes sequences was depicted in Fig. 3.

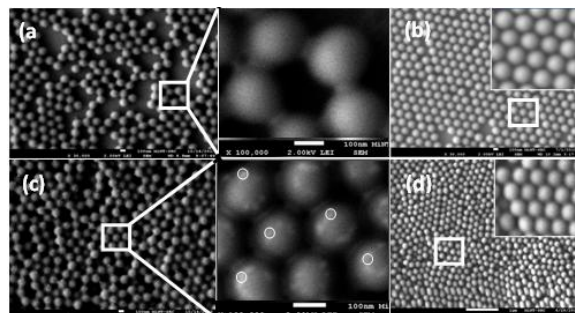


Figure 1. FESEM images of surface morphology of Cd metal particles-covered PSNs (a), pristine PSNs (b), Cd metal particles-covered PSNs irradiated by continues laser (c) and pristine PSNs irradiated by continues laser (d).

In Fig.1 (a) and (c) show the different concentration of metal precursor, where in Fig. 1(c), a much higher concentration of metal precursor was introduced. Figure 1 (b) is bare PSNs compared to 1(c) exposed to laser beam for 20 minutes. The Fig. 1 (c) shows the Cd metal particles might have fully covered the surface of PSNs reducing the laser impact to it shape, where bare PSNs will usually deformed under laser treatment.

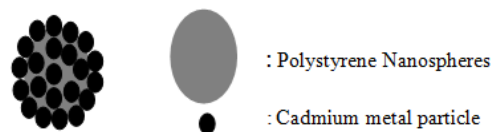


Figure 2. Proposed model of Cd metal particles-covered PSNs body constructed up PSNs-based material thin film

ATR-FTIR spectra:

Comparing Fig.3(b) to Fig.3(c) we assumed the Cd metal particles might fully-covered the polystyrenes surface, since its wave number peak pattern slightly changed. Unfortunately this position was likely lack of advantage due to it could not prevent the bonds from laser exposure as its ATR-FTIR spectrum in ranging wave number bands of 3080-2920 cm^{-1} was disappeared followed by continuous laser exposed for 20 minutes as shown in Fig. 3(c). Thus, hydrogen atoms of polystyrenes phenyl moieties collapsed during laser exposure. This situation lead to the formation of a reactive molecular ionic radical which drove the according phenyl intra-molecule degradations progressed since it was justified by disappearing wave number peak of around 1600 cm^{-1} which was commonly attributed, in this case, to the phenyl ring. $\text{C}=\text{Csp}^2$ stretching vibration as shown in Fig.3(a).

In contrast, however it was surprise that ATR-FTIR spectrum of around 790 cm^{-1} , 699 cm^{-1} and 668 cm^{-1} represented the bending; wagging and twisting vibration of C-ph bonds (ph stands for phenyl moiety) was still generated from the Cd metal particles-covered PSNs thin film during the laser exposure as it can be seen in Fig.3(a). It attributed that probable the aromatic ring of phenyl moiety actually did not totally destructed but it was just transformed to be non-aromatic one during the laser exposure. This possibility was clearly confirmed by its surface morphology image that kept

in spherical shape as shown in Fig.2(e). This phenomenon might be very unique due to the Cd metal particles settled therein could act as a shield that prevent covalent bonds collapsed by laser irradiation.

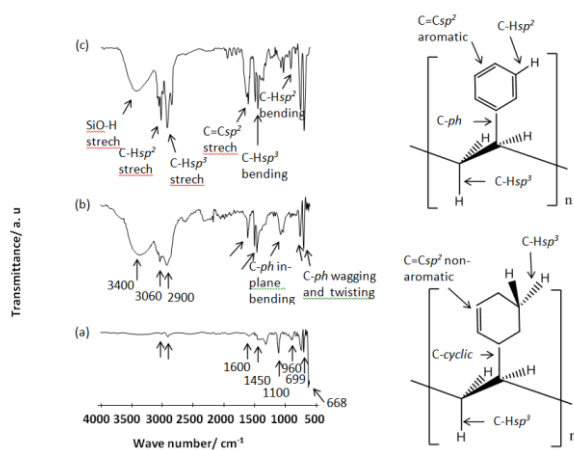


Figure 3. ATR-FTIR spectra of Laser-exposed Cd metal particles-covered PSNs (a), Cd metal particles-covered PSNs (b) and pristine PSNs (c). These spectra were analyzed under the sequence modes of Tune-Up, ATR correction, Base line correction and Normalization and quoted from reference [22] for spectra (b) and (c). **Right:** Rough sketch of Polystyrene unit molecular structure.

Conclusions:

It was concluded that the basic molecular structure of polystyrene framework constructed up the fabricated Cd-CPSNs thin film material was not change significantly compared to that of pristine PSNs. The existence of Cd metal particles covered the surface of PSNs could provide at least two impacts especially to its physical properties, those are (1) made capable to form a dumbbell-like structure between two Cd particles-covered PSNs adjacent, and (2) enhancing the porosity of the PSNs-constructed material compare to the pristine PSNs. The most important and interesting phenomenon was the existence of Cd metal particles on the PSNs surface might act selectively as a shield to prevent certain atomic bonds of polystyrene framework towards continuous laser light irradiation of 632 nm wavelength for 20 minute exposure. This research was successfully performed since the proposed model of Cd-CPSNs as depicted in Fig.2 could be created.

Acknowledgments:

Thank you to the support given by Universiti Tun Hussien Onn Malaysia (UTHM), MiNT-SRC UTHM, and the director of Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia for the technical and chemicals support.

References :

[1]Tseng C.C, Chang C.P, Ou J.L, Sung Y, Ger M.D. 2008. The preparation of metal-styrene oligomer and metal-SSNa nanocomposites through single thermal process. *Colloidal and Surface A: Physicochem. Eng. Aspects* 330: 42-48
 [2]Wang Xian-Yong and Weck Marcus. 2005. Poly(styrene)-Supported Alq3 and BPh2q. *Macromolecules* 38: 7219-7224
 [3]Kamrupi I.R, Phukon P, Konwer B.K, Dolui S.K. 2011. Synthesis of silver-polystyrene nanocomposite particles using water in supercritical carbon dioxide medium and its antimicrobial activity, *The Journal of Supercritical Fluids*, 55: 1089-1094
 [4]Shi Donglu, Cho Hoon Sung, Chen Yan, Xu Hong, Gu Hongchen, Lian Jie, WangWei, Liu Guokui, Huth Christopher, Wang Lumin., Ewing Rodney C, Budko Sergei, Pauletti Giovanni M, Dong Zhongyun. 2009. Fluorescent.
 [5]Polystyrene-Fe3O4 Composite Nanospheres for In Vivo Imaging and Hyperthermia, *Adv. Mater.* 21: 2170-2173.

[6]Wang Limei, Wang Fujun, Chen Dajun. 2008. Fabrication and characterization of silver/polystyrene nanospheres with more complete coverage of silver nano-shell, *Materials Letters* 62: 2153-2156.
 [7]Chen Ying, Cho Juhee, Young Alex, Taton T Andrew. 2007. Enhanced Stability and Bioconjugation of Photo-cross-linked Polystyrene-Shell, Au-Core Nanoparticles, *Langmuir* 23(14): 7491-7497.
 [8]Astilean S, Bolboaca M, Maniau D, Iliescu T. 2004. Ordered Metallic Nanostructures for Surface Enhance Raman Spectroscopy, *Romanian Reports in Physics*, 56(3): 346 - 351.
 [9]Moyo Mambo, Okonkwo Jonathan O, Agyei Nana M. 2012. Recent Advances in Polymeric Materials Used as Electron Mediators and Immobilizing Matrices in Developing Enzyme Electrodes, *Sensors* 12, 2012: 923-953.
 [10]Jamois Cécile, Li Cheng, Gerelli Emmanuel, Orobchouk Régis, Benyattou Taha, Belarouci Ali, Chevotot Yann, Monnier Virginie, Souteyrand Eliane. 2011. New Concepts of Integrated Photonic Biosensors Based on Porous Silicon, *Biosensors-Emerging Materials and Applications*, InTech, Ch.14, 2011: 265-290.
 [11]Sarmaa Anil Kumar, Vatsyayanb Preety, Goswami Pranab, Minteerc Shelley D. 2009. Recent advances in material science for developing enzyme electrodes, *Biosensors and Bioelectronics* 24: 2313-2322.
 [12]Cheng Cheanyeh, Huang Zhu-Ming, Chung Wen-Yaw, Pijanowskad Dorota G, Dawguld Marek. 2012. Development of Polymeric Resin Ion-exchanger Based Chloride Ion-selective Electrode for Monitoring Chloride Ion in Environmental Water, *J. Chin. Chem. Soc.* 59: 122-131.
 [13]Moura Ruan C.A, Bertuol Daniel A, Ferreira Carlos A, Amado Franco D.R. 2012. Study of Chromium Removal by the Electrodialysis of Tannery and Metal-Finishing Effluents, *International Journal of Chemical Engineering*: 1-7.
 [14]Šljukić Biljana, Morais Ana L, Santos Diogo M. F, Sequeira César A C. 2012. Anion-or Cation-Exchange Membranes for NaBH₄/H₂O₂ Fuel Cells, *Membranes* 2: 478-492.
 [15]Charoenmark Lalida, Polpanich Duangporn, Thiramanas Raweewan, Tangboriboonrat Pramuan. 2012. Preparation of Superparamagnetic Polystyrene-Based Nanoparticles Functionalized by Acrylic Acid, *Macromolecular Research*, 20 (6):590-596.
 [16]Pellach Mechal and Margel Shlomo. 2011. The encapsulation of an amphiphile into polystyrene microspheres of narrow size distribution, *Chemistry Central Journal*, 5: 78.
 [17]Ward Mark A and Georgiou Theoni K. 2011. Thermoresponsive Polymers for Biomedical Applications, *Polymers* 3:1215-1242.
 [18]Nyström Anderas M. and Wooley Karen L. 2008. Thiol-functionalized shell crosslinked knedel-like (SCK) nanoparticles: A versatile entry for their conjunction with biomacromolecules, *Tetrahedron* 64(36): 8543-8552.
 [19]Nakajima Kiyotaka and Hara Michikazu. 2012. Materials and Structures Laboratory, Tokyo Institute of Technology, *ACS Catal.*, 2(7):1296-1304.
 [20]Gu Xuefeng, Qiu Teng, Zhang Wenjun, Chu Paul K. 2011. Light-emitting diode enhanced by localized surface Plasmon resonance, *Nanoscale Research Letters* 6:199.
 [21]Scarmagnani Silvia, Walsh Zarah, Slater Conor, Alhashimy Nameer, Paull Brett, Macka Mirek, Diamond Dermot. 2008. Polystyrene bead-based system for optical sensing using spiropyran photoswitches, *J. Mater. Chem.*, 18: 5063-5071.
 [22]Qua Jian-Bo, HuangYong-Dong, Jing Guang-Lun, Liu Jian-Guo, Zhou Wei-Qing, Zhua Hu, Lua Jian-Ren. 2011. A novel matrix derivatized from hydrophilic gigaporous polystyrene-based microspheres for high-speed immobilized-metal affinity chromatography, *Journal of Chromatography B*, 879: 1043-1048.
 [23]Wibawa Pratama Jujur, Saim Hashim, Agam Mohd. Arif, Nur Hadi. 2011. Design, Preparation and Characterization of Polystyrene Nanospheres Based-Porous Structure towards UV-Vis and Infrared Light Absorption, 2011 International Conference on Physics Science and Technology (ICPST 2011), *Physics Procedia* 22: 524 - 531.
 [24]Shiju Raveendran N and Guliants Vadim V. 2009. Recent developments in catalysis using nanostructured materials, *Applied Catalysis A: General* 356: 1-17.
 [25]Djakovitch Laurent, Batail Nelly, Genelot Marie. 2011. Recent Advances in the Synthesis of N-Containing Heteroaromatics via Heterogeneously Transition Metal Catalysed Cross-Coupling Reactions, *Molecules*, 16: 5241-5267.
 [26]Hickner Michael A, Ghassemi Hossein, Kim Yu Seung, Einsla Brian R, McGrath James E. 2004. Alternative Polymer Systems for Proton Exchange Membranes (PEMs), *Chem. Rev.* 104: 4587-4612
 [27]Wibawa Pratama Jujur, Agam Mohd. Arif, Nur Hadi, Saim Hashim. 2010. 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*, 1341: 54-61