

Synthesis and characterization of metal organic framework based on copper particles for storage of zinc oxide nanoparticles

P. Mehrani, N.Ghasemi*, M.Ramezani

Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran

Submitted March 24, 2016; Accepted August 8, 2016

Handled studies show that organic-metal frameworks are as new group from Nano material for storing and separating materials and chemical compounds. This group is attracted attention from porous compounds in recent ten years that because of big size of their holes, their high area, selective attraction of small molecules and optical or magnetic responses in presence of guest molecules. MOFs by collection of ions or metal clusters are made as Coordination Complexes and organic ligands as organic connectors of metal ions. This group has special physical and chemical materials and they are arranged from structure view. In this study of Nano particles of zinc oxide and MOFs based on copper were prepared and by methods FT-IR (Fourier transformation-infrared spectrometer), SEM (Scanning electron microscope), XRD (X-Ray Diffraction) were recognized and then recognition way of MOFs were investigated. At last Nano particles ZnO in porous space of MOFs was synthesized and image of SEM as final compound was proved that metal organic framework madding from suitable copper for Nano particle of ZnO

Keywords: Metal Organic Frameworks (MOFs), NanozincOxide, Storing chemical compounds

INTRODUCTION

Nano sized particles of semiconductor materials have gained much more interest in recent years due to their desirable properties and applications in different areas such as catalysts [1], sensors [2], photoelectron devices [3,4], highly functional and effective devices [5]. These Nanomaterials have novel electronic, structural, and thermal properties which are of high scientific interests in basic and applied fields. Zinc oxide (ZnO) is a wideband gap semiconductor with an energy gap of 3.37 eV at room temperature. It has been used considerably for its catalytic, electrical, optoelectronic, and photochemical properties [6-9]. ZnO Nanostructures have a great advantage to apply to a catalytic reaction process due to their large surface area and high catalytic activity [10]. Since zinc oxide shows different physical and chemical properties depending upon the morphology of Nanostructures, not only various synthesis methods but also the physical and chemical properties of synthesized zinc oxide are to be investigated in terms of its morphology. Many methods have been described in the literature for the production of ZnO Nanostructures such as laser ablation [11], hydrothermal methods [12], electrochemical depositions [13], sol gel method [14], chemical vapor deposition [15], thermal decomposition [16], and combustion method [17,18]. Recently, ZnO Nanoparticles were prepared by ultrasound [19], microwave-assisted combustion method [20], two-step mechanochemical-thermal synthesis [21],

anodization [22], co-precipitation [23], and electrophoretic deposition [24].

Zinc oxide, with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photo stability, is a multifunctional material [25,26]. In materials science, zinc oxide is classified as a semiconductor in group II-VI, whose covalence is on the boundary between ionic and covalent semiconductors. [27,28]. The piezo- and pyro electric properties of ZnO mean that it can be used as a sensor, converter, energy generator and photo catalyst in hydrogen production [29,30]. Because of its hardness, rigidity and piezoelectric constant it is an important material in the ceramics industry, while its low toxicity, biocompatibility and biodegradability make it a material of interest for biomedicine and in pro-ecological systems [31–33]. The variety of structures of Nano metric zinc oxide means that ZnO can be classified among new materials with potential applications in many fields of Nanotechnology. Zinc oxide can occur in one- (1D), two- (2D), and three-dimensional (3D) structures. One-dimensional structures make up the largest group, including Nano rods [34–36], -needles [37], -helixes, -springs and -rings [38], -ribbons [39], -tubes [40–42] -belts [43], -wires [44–46] and -combs [47]. Zinc oxide can be obtained in 2D structures, such as Nano plate/nan sheet and Nano pellets [48,49]. Examples of 3D structures of zinc oxide include flower, dandelion, snowflakes, coniferous urchin-like, etc. [50–53].

ZnO provides one of the greatest assortments of varied particle structures among all known materials.

MOFs are crystal compounds but with low density that have two units of metal ion or cluster as

* To whom all correspondence should be sent

E-mail: N-ghasemi@iau-arak.ac.ir

knot and organic ligand as connector. These materials can synthesize in environment temperature to 220 °C and with pressures between zero to 20 atmosphere and pH between 1-10. During recent fifteen years, studies on MOFs were developed and it is as a new issue in crystal engineering of chemistry and material science. Physical and chemical features involving MOFs shows them as a suitable one for storing and separating chemical compounds. Because of following reasons, the best sample is applications such as attraction and separating chemical compounds:

- The area of high level (to some extent 6000 g/m³) causes that organic connectors will be available and causes increasing attraction rate of guest molecules.
- Crystal nature of MOFs provides computer modeling with high care for prediction of linked places of quest molecules .
- A wide range of organic ligands and different synthesis methods can provide possibility for designing MOFs that can optimize physical and chemical features.

Metal-organic frameworks (MOFs) are being investigated as potential materials for a variety of applications including gas storage, [54–59] gas separation, [60–62]. catalysis,[63-65].sensors,[66–68].and drug delivery[69–71].

Because of this reason, in this study it is tried that after synthesizing Nano particles ZnO, MOFs will be prepared based on copper metal and at last Nano particles ZnO is stored among porous structure MOF.

EXPERIMENTAL

Materials and methods

All materials and solvents used in the synthesis of nano-zinc oxide and Nano metal organic frameworks were purchased from Sigma Aldrich and Merck and used without any further purification. Infrared spectra were recorded as KBr disks on Tensor 27 Bruker spectrophotometer. The evaluation of MOF and synthesized Nano ZnO were monitored by powder X-ray diffraction Philips PW 1800 diffractometer with Cu K α radiation. Scanning electron microscopy measurements was performed on a VEGA\\TESCAN at an accelerating voltage of 15 kV.

For preparation of ZnO particle, at first 6 g (Zn (NO)₃.7 H₂O) is dissolved in 50 mm deionized water and another dish 6 g Thiourea is dissolved in 50 mm deionized water. Then contents of two dishes will be refluxed in 72 hours. After refluxing white sediment, it will be filtered with deionized water by four micron filter. Now prepared material is placed about three hours in an oven with 500 °C and made particles are recognized by SEM and XRD methods.

Synthesis of nano metal organic frameworks

For making MOF at first it is dissolved in a 6 g dish Cu (NO₃)₂.3 H₂O in 20 mm deionized water and also in another 6 g dish benzene-1.3.5-tricarboxylic in 3 mm Dimethylformamide (DMF) and 3 mm Methanol about 20 min in temperature 30 °C on magnetic mixer till it will be dissolved well. Then contents of two dishes are mixed and then we placed them in auto clave as 72 hours in 280 °C. At last auto clave contents is filtered three times and resulted sediment placed in an oven three hours in 280 °C. Now MOFs is made and for recognizing it, we use methods of XRD, SEM,FT.IR.

Method of placing nano particle ZnO on MOF

In this stage we use proportion 1 to 3 from synthesized Nano particles ZnO and MOF. Then we dissolve 3 g of MOF in 5 mL and in other dish we add 1 g Nano particles ZnO in 5 mL to shape a paste form about 5 min under alter ultrasonic to be mixed well. Then dish involving ZnO we put a paste on stirrer in temperature 60 °C and contents of dish including MOF will be added to it drop by drop. Mixing process needs 30 min till resulting material will be completely dry and its ethanol will be removed. Now Nano particle ZnO is placed among holes of MOF and this issue is observable in images of SEM and XRD.

Characterization of ZnO nanoparticles

The typical powder XRD pattern of ZnO Nano particles is given in Fig. 1. All the diffraction peaks are well indexed to the hexagonal ZnO wurtzite structure (01-075-0576/ 96 Zinc Oxide). Diffraction peaks corresponding to the impurity were not found in the XRD patterns, confirming the high purity of the synthesized product.

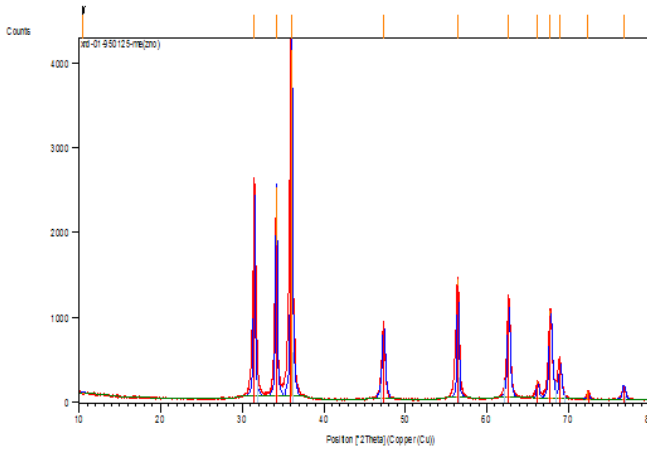


Fig. 1. XRD pattern of ZnO Nanoparticles

Scanning electron microscopic analysis (SEM) on Zinc Oxide Nanoparticles was shown in Figure 2. As is clear, the magnesium hydroxide Nano particles have a good and uniform distribution.

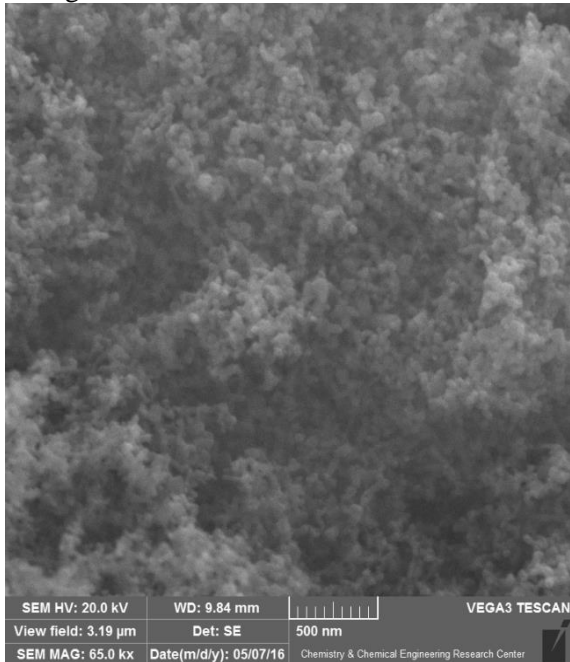


Fig. 2. SEM images of ZnONanoparticles

Characterization of metal organic frameworks (MOF)

The typical powder XRD pattern of metal organic frameworks based on copper metal is given in Figure 3. All the diffraction peaks are well indexed to (00-032-0324 and 00-012-0782).

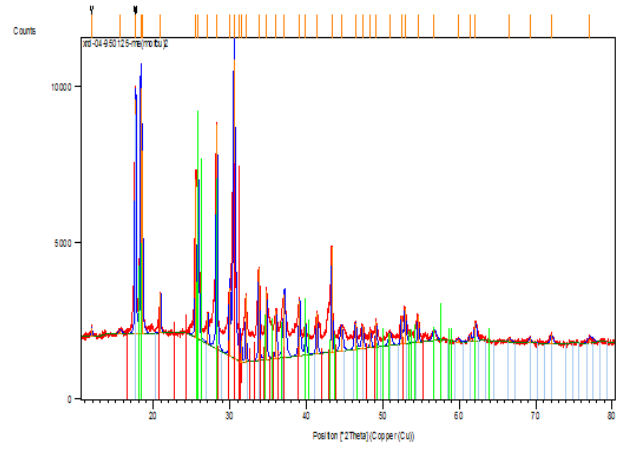


Fig. 3. XRD pattern of metal organic frameworks

Scanning electron microscopic analysis (SEM) on metal organic frameworks (MOF) was shown in Figure 4. As is clear, the MOF Nano particles have a good and uniform distribution. Also in this picture porous space of metal organic frameworks is observable for storing Nano particles ZnO.

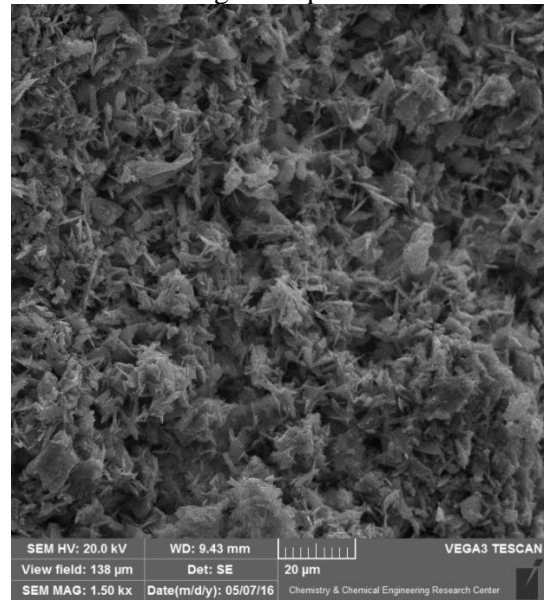


Fig. 4.SEM image of metal organic frameworks (MOF)

Characterization of metal organic frameworks (MOF) and Zinc Oxide Nanoparticles

The typical powder XRD pattern metal organic frameworks (MOF) and Zinc Oxide Nanoparticles is given in Fig. 5. All the diffraction peaks are well indexed to the (01-075-0576 and 00-032-0324).

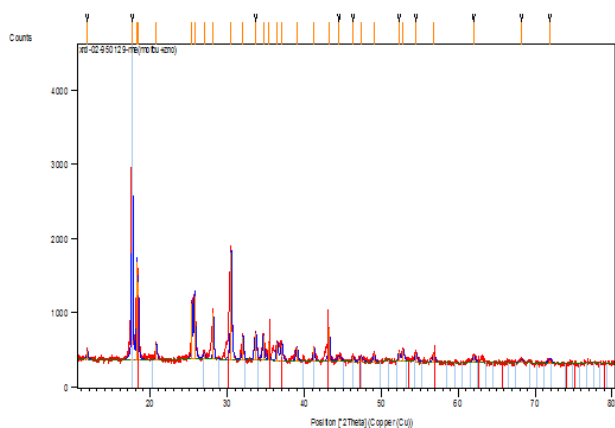


Fig. 5. XRD pattern of metal organic frameworks and zinc oxide nano particles

Scanning electron microscopic analysis (SEM) on metal organic frameworks (MOF) and Zinc Oxide Nanoparticles was shown in figure 6. In this picture, the way of placing Nano particles Zn o in porous space of MOF is showed.

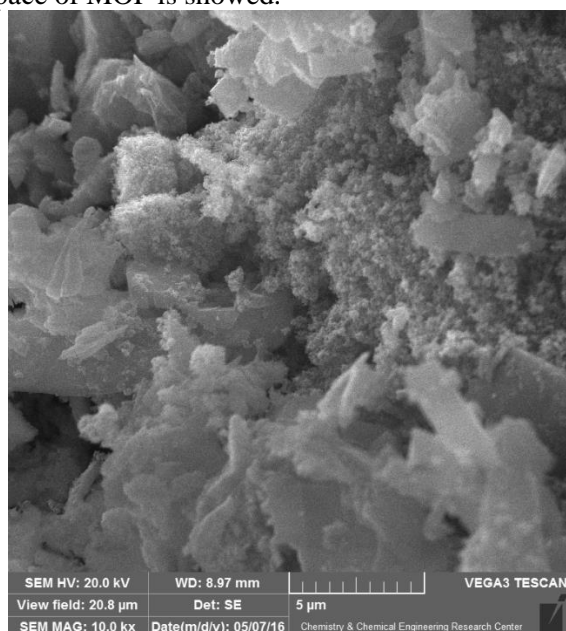


Fig. 6. SEM image of metal organic frameworks (MOF) and zinc oxide nanoparticles

RESULTS AND DISCUSSION

In recent years, investigations related to structures with metal-organic frameworks, MOF is considered very much. The importance of these compounds is related to simple path of synthesis, having geometric building and multiple molecule structures and different applications such as surface attraction and storing chemical compounds, luminescence, nonlinear optical features, magnetic features, ion exchange, catalyst features and pharmaceutical features. MOFs structures involving building units of molecules as cluster of metal ions and organic connectors and it is a growth situation in

chemistry. In this study, it is tried that synthesized ZnO Nano particle is stored in porous MOF space based on copper metal. The purpose of this study is need of this group to store ZnO for attracting cyanide from wastes that based on preparation of suitable MOF for storing ZnO, the possibility of continuing research of related experiments is provided.

REFERENCES

1. S.S. Joshi, P.R. Patil, M.S. Naimase, A. Bakare, *J. Nanopart. Res.* **5**, 635 (2006).
2. X.L. Cheng, H. Zhao, L. H. Huo, S. Gao, X. Zhao, *Sens. Actuators B.* **102**, 248 (2004).
3. S. Y. Lee, E. S. Shim, H. S. Kang, *Thin Solid Films.* **437**, 31 (2005).
4. Z. L. Wang, X. Y. Kong, Y. Ding, P. Gao, W. L. Hughes, *Adv. Funct. Mater.*, **14**, 943 (2004).
5. Y. H. Huang, Y. Zang, L. Liu, S. S. Fan, Y. Wei, *J. Nanosci. Nanotechnol.* **6**, 787 (2006).
6. D. Brida, E. Fortunato, I. Ferreira, H. Aguas, T. Martins, *J. Non-Cryst. Solids.*, **299**, 1272 (2002).
7. J. Wang, *J. Phys. Condens. Matter.* **16**, R829 (2004).
8. M. Suche, S. Christoulakis, K. Moschovis, N. Katsarakis, S. Kiriakidis, *Thin Solid Films.* **515**, 551 (2006).
9. A. Ashour, M. A. Kaid, N. Z. El-Syed, H. Ibrahim, *Appl. Surf. Sci.* **252**, 7844 (2006).
10. J. C. Chen, J. Tang, *J. Hazard. Mater.* **142**, 88–96 (2007).
11. N. Scarisoreanu, D. G. Metai, G. Dinescu, G. Epurescu, C. Ghica, L. C. Nistor, F. Dinescu, *Appl. Surf. Sci.* **247**, 518 (2005).
12. Y. H. Ni, X. W. Wei, J. M. Hong, L. Ye, *Mater. Sci. Eng., B, Solid State Mater. Adv. Technol.* **121**, 42 (2005).
13. S. Chang, S. O. Yoon, H. J. Park, L. Sakai, *Mater. Lett.* **53**, 432 (2002).
14. M. Ristiuc, S. Musiac, M. Ivanda, D. Popoviac, *J. Alloys Compd.* **397**, L1–L4 (2005).
15. J. J. Wu, Q. Liu, *Adv. Mater.* **14**, 215 (2002).
16. R. C. Wang, Q. Tsai, *Appl. Phys. A.* **94**, 241 (2009).
17. D. G. Lamas, G. E. Lascarea, D. M. Walsoc, *J. Eur. Ceram. Soc.* **18**, 1217 (1998).
18. S. Badhuri, F. Badhuri, *Nanostrect. Mater.* **8**, 755 (1997).
19. Z. Khorsand, A. Abid, W. H. Majid, H. Z. Wang, R. Yousefi, M. Golsheikh, F. Ren, *Ultrasonic Sonochemistry*, **20**, 395 (2013).
20. M. Kooti, N. Sedish, *J. Chem.* **12**, 34–56 (2013).
21. D. Rajesh, B. Vara Lakshmi, S. Sunandana, *Physica B-Cond. Mater.*, **407**, 4537 (2012).
22. A. Shetty, S. Nanda, *Appl. Phys. A.*, **109**, 151 (2012).
23. O. Singh, N. Kohli, K. Singh, *Sens. Actuators B.* **178**, 149–154 (2013).
24. A. Vazquez, I. A. Lopez, S. Gomez, *J. Mater. Sci.* **48**, 2701 (2013).
25. D. Segets, J. Gradl, R. K. Taylor, K. Vassilev, *Solubility and Surf. Energ. ACS Nano*, **3**, 1703 (2009).
26. X. Lou, *J. Sens. Trans. Technol.*, **3**, 1 (1991).

27. E. Bacaksiz, M. Parlak, M. Tomakin, O. Özcelik, *J. Alloy. Compd.*, **466**, 447 (2008).
28. J. Wang, J. Cao, B. Fang, P. Lu, S. Deng, H. Wang, *Mater. Lett.*, **59**, 1405 (2005).
29. Z. L. Wang, *ACS Nano*, **2**, 1987 (2008).
30. M. Chaari, A. Matoussi, *Phys. B Condens. Matter*, **407**, 3441 (2012).
31. Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M. A> Reshchikov, S. Doğan, V. Avrutin, S. J. Cho, H. Morkoç, *J. Appl. Phys.*, **98**, 25-35 (2005).
32. S. Bhattacharyya, A. Gedanken, *Microporous Mesoporous Mater.*, **110**, 553 (2007).
33. B. Ludi, M. Niederberger, *Dalton Trans.*, **42**, 12554 (2013).
34. D. Banerjee, J. Y. Lao, D. Z. Wang, J. Y. Huang, Z. F. Ren, D. Steeves, B. Kimball, M. Sennett, *Appl. Phys. Lett.*, **83**, 2061(2003).
35. Y. B. Hahn, *Korean J. Chem. Eng.* 2011, **28**, 1797 (2011).
36. H. Mahabadipour, and H. Ghaebi, *Appl. Therm. Eng.* **50**, 771-780 (2013).
37. R. Wahab, S. G. Ansari, Y. S. Kim, H. K. Seo, H. S. Shin, *Appl. Surf. Sci.*, **253**, 7622 (2007).
38. X. Kong, Y. Ding, R. Yang, Z. L. Wang, *Science*, **303**, 1348 (2004).
39. Z. W. Pan, Z. R. Dai, Z. L. Wang, *Science*, **291**, 1947 (2001).
40. A. Hamidi, and S. Jedari, *Sharif. Civ. Eng. J.* **29**, 29-35 (2011).
41. W. J. Chen, W. L. Liu, S. H. Hsieh, T. K. Tsai, *Appl. Surf. Sci.*, **253**, 6749 (2007).
42. J. Liu, X. Huang, J. Duan, H. Ai, P. Tu, *Mater. Lett.* 2005, **59**, 3710 (2005).
43. Y. Huang, J. He, Y. Zhang, Y. Dai, Y. Gu, S. Wang, C. Zhou, *J. Mater. Sci.*, **41**, 3057 (2006).
44. B. Nikoobakht, X. Wang, A. Herzing, Z. Shi, *Chem. Soc. Rev.*, **42**, 342 (2013).
45. L. C. Tien, S. J. Pearton, D. P. Norton, F. Ren, *J. Mater. Sci.*, **43**, 6925 (2008).
46. J. Cui, *Mater. Charact.*, **64**, 43 (2012).
47. T. Xu, P. Ji, M. He, J. Li, *J. Nanomater.* **32**, 34-65 (2012).
48. W. S. Chiuva, P. S. Khiew, M. Clokea, D. Isaa, T. K. Tana, S. Radimanb, R. Abd-Shukorb, M. A. Abd-Hamid, N. M. Huangc, H. N. Limd, *Chem. Eng. J.*, **158**, 345 (2010).
49. M. Jose-Yacaman, C. Gutierrez-Wing, M. Miki, D. Q. Yang, K. N. Piyakis, E. Sacher, *J. Phys. Chem.*, **109**, 9703 (2005).
50. V. Polshettiwar, B. Baruwati, M. Varma, *ACS Nano*, **3**, 728 (2009).
51. Q. Xie, Z. Dai, J. Liang, L. Xu, W. Yu, Y. Qian, *Solid State Commun.*, **136**, 304 (2005).
52. J. Liu, X. Huang, Y. Li, K. M. Sulieman, F. Sun, X. He, *Scr. Mater.*, **55**, 795 (2006).
53. M. Bitenc, Z. C. Orel, *Mater. Res. Bull.*, **44**, 381 (2009).
54. B. Panella, M. Hirscher, *Adv. Mater.*, **17**, 538 (2005).
55. M. P. Suh, H. J. Park, T. K. Prasadand, D. W. Lim, *Chem. Rev.*, **112**, 725 (2012).
56. A. C. McKinlay, B. Xiao, D. S. Wragg, P. S. Wheatley, I. L. Megsonand, R. E. Morris, *J. Am. Chem. Soc.*, **130**, 10440 (2008).
57. A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Cote, J. Kim, O. M. Yaghi, *J. Am. Chem. Soc.*, **127**, 7110 (2005).
58. T. Duren, O. M. Sarkisov, R. Q. Yaghiand, W. Snurr, *Langmuir*, **20**, 2683 (2004).
59. K. L. Kauffman, J. T. Culp, A. J. Allen, L. Espinal, W. Wong-Ng, T. D. Brown, A. Goodman, M. P. Bernardo, R. J. Pancoast, D. Chirdon, C. Matranga, *Angew. Chem., Int. Ed.*, **50**, 10888 (2011).
60. Y. S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp, R.Q. Snurr, *Langmuir*, **24**, 8592 (2008).
61. B. Wang, A. P. Cote, H. Furukawa, M. O’Keeffe, O. M. Yaghi, *Nature*, **453**, 207 (2008).
62. R. Babarao, Z. Q. Hu, J. W. Jiang, S. Chempathand, S. I. Sandler, *Langmuir*, **23**, 659 (2007).
63. P. Pianko-Oprych, and S. Hosseini, *Energies*. **10**, 2103 (2017).
64. S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Suand, W. Wang, *J. Am. Chem. Soc.*, **133**, 19816 (2011).
65. K. K. Tanabe, S. M. Cohen, *Angew. Chem., Int. Ed.*, **48**, 742 (2009).
66. F. X. L. I. Xamena, A. Abad, A. Corma, H. Garcia, *J. Catal.*, **250**, 294 (2007).
67. D. N. Dybtsev, A. L. Nuzhdin, H. Chun, K. P. Bryliakov, E. P. Talsi, V. P. Fedin, K. Kim, *Angew. Chem., Int. Ed.*, **45**, 916 (2006).
68. B. L. Chen, Y. Yang, F. Zapata, G. N. Lin, G. D. Qianand E. B. Lobkovsky, *Adv. Mater.*, **19**, 1693 (2007).
69. J. He, K. K. Yee, Z. T. Xu, M. Zeller, A. D. Hunter, S. S. Y. Chuiand, C. M. Che, *Chem. Mater.*, **23**, 2940 (2011).
70. G. Lu, O. K. Farha, L. E. Kreno, P. M. Schoencker, K. S. Walton, R. P. Van Duyne, J. T. Hupp, *Adv. Mater.*, **23**, 4449 (2011).
71. K. L. Wong, G. L. Law, Y. Y. Yang, W. T. Wong, *Adv. Mater* ,**18**, 1051 (2006).
72. P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur ,G. Ferey, R. E. Morris, C. Serre, *Chem. Rev.*, ,**112**, 1232 (2012).
73. A. C. McKinlay, R. E. Morris, P. Horcajada, G. Ferey, R. Gref, P. Couvreur, C. Serre, *Angew. Chem., Int. Ed.*, **49**, 6260 (2010).
74. R. Zou, Amr I. Abdel-Fattah, H. Xu, Y. Zhao, D.D. Hickmott, *Cryst. Eng. Comm*, **12**.1337 (2010).