Nanohardness Properties of MOF-199 Synthesized Using Facile Method as Bulk Adsorbents and Screen-Printed Thin-Film

Muhammad Faizulizwan Mohamad Fadli[1], Siti Zubaidah Othman[1], Ooi Jen Wai[1], Nowshad Amin[2], Akihiko Matsumoto[3], and Halina Misran[2(✉)]

[1] Nanoarchitectonic Laboratory, Department of Mechanical Engineering, Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, 43000 Kajang, Selangor, Malaysia
mfaizulizwan@uniten.edu.my

[2] Institute of Sustainable Energy, Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, 43000 Kajang, Selangor, Malaysia
halina@uniten.edu.my

[3] Department of Environmental and Life Sciences, Toyohashi University of Technology, Toyohashi 441-8580, Japan

Abstract. This paper reports on the nanohardness properties of copper-based metal-organic framework (MOF-199) synthesized in-house by facile method fabricated into bulk adsorbents by binder-less compression and into thin-film by screen-printing. 13 mm diameter bulk adsorbents were prepared for four different materials 1) MOF-199, 2) zeolite 13X, 3) activated carbon (AC) and 4) hybrid MOF-199: AC (1:1). In addition, MOF-199 was fabricated into thin-film on soda-lime glass substrates using screen-printing method. Polyvinyl acetate (PVA) was replaced with environmental-friendly binder materials of gum Arabic (gA) and palm oil based fatty alcohol (PODFA) with 8 carbon chain of decyl alcohol. X-ray diffraction (XRD) analyses of MOF-199 fabricated both by binder-less compression and screen-printing exhibited a prominent peak at ca. $2\theta = 11.7°$ attributable to (222) reflection plane of octahedral crystal structure suggesting that morphology and crystallinity were retained after fabrication processes. The octahedral morphology at ca. 1 µm and ca. 2 µm were observed for screen-printed thin film suggesting that the structure was preserved. Reduced modulus (R*) for pure MOF-199 and hybrid MOF-199:AC bulk adsorbents were at ca. 2.818 GPa and 0.002 GPa, respectively suggesting that hybrid adsorbent was not suitable for applications due to lack of hardness. Reduced modulus value of MOF-199 thin-film were higher at ca. 6.577 GPa (gA), 3.539 GPa (PVA), and 0.816 GPa (PODFA), respectively.

Keywords: MOF-199 · Binderless · Screen-printing · Thin-film · Nanohardness

1 Introduction

Fossil fuel-fired power plants and natural gas combine cycle power plant are two common power plants in energy generation [1]. Carbon dioxide (CO_2) emission from power

S. Samion et al. (Eds.): MITC 2020, LNME, pp. 80–85, 2022.
https://doi.org/10.1007/978-981-16-9949-8_15

plant generation produced ca. 40% of the total emission of greenhouse gases. These can be mitigated by carbon capture and storage as well as utilization (CCUS) technology [2]. Reduction of CO_2 emission can be done by various method especially physical adsorption using pressure swing adsorption method (PSA) which requires highly porous adsorbents with mechanical stability to withstand high pressure at the gas inlet. Various porous materials were used as adsorbents such as zeolites 13X, activated carbon (AC) and recently, metal-organic framework (MOFs) materials.

Recently, metal-organic frameworks (MOFs) are popular as a new class of nanoporous crystalline material consist of metal ions and organic ligand to form porous and flexible structure. Therefore, thorough understanding of mechanical properties such as bulk modulus, shear modulus, Young's modulus, linear compressibility, and Poisson's ratio are important factors and necessary in the post-synthetic processing of MOFs. These knowledge has wide implications in order for successful transition of the materials from laboratory scale to industrial applications. Thus, tn this study, copper-based MOF materials synthesized in-house using facile method was fabricated into bulk adsorbents as well as thin film and their nanohardness properties investigated to be applied in various industrial applications.

2 Experimental Methods

2.1 Materials

The adsorbents powder used in this study MOF-199, 13X (bead, 2–8 mesh, Sigma Aldrich), commercial-grade activated carbon (AC) and gum Arabic (gA), ethanol (synthesis grade, HmbG Chemical), polyvinyl acetate (PVA, Sigma Aldrich), octyl alcohol (PODFA, C8, Emery Oleochemical). All chemicals were used in as-received condition.

2.2 Fabrication

Adsorbent materials in powder form were compressed at four different pressure, 74 MPa, 110 MPa, 148 MPa, and 222 MPa to obtain a round bulk-shaped adsorbent using hydraulic compression machine (Carver) in 13 mm diameter cylindrical die while maintaining the mass at ca. 0.5 g with 5 min holding time. Zeolite 13X and AC were heated at 373 K overnight to remove moisture content. Hybrid adsorbent of MOF-1990:AC were physically mixed at 1:1 ratio. MOF-199 was made into paste with gum A(gA), polyvinyl acetate (PVA) and PODFA as binder to be screen-printed on soda lime glass substrate (2 cm^2). Substrate was rinsed with ethanol solution and sonicated for 15 min and washed with distilled water prior to screen orienting process. MOF-199 paste was prepared by adding 5 drops of binder solutions into ca. 0.1 g of MOF-199 powder to obtain well-blend paste to coat on targeted area by mesh using a squeegee. Then, MOF-199 thin-films were dried in room temperature.

2.3 Structural Characterization

The as-compressed adsorbents without binder were characterized by X-ray diffraction analyses (XRD), field emission scanning electron microscopy (FESEM) and nanoindentation. XRD patterns were obtained using Shimadzu XRD-6000 from 5°–45° at 30 kV, 20 mA, scan step 0.02° and scan speed 3°/min. Morphology of bulk-shaped adsorbents was observed from FESEM images using SU8030 Hitachi at acceleration voltage of 1 kV. Nanoindentation using Hysitron TriboIndenter (TI 950 TriboIndenter) with 10 times loading and unloading at different location of the surface area of bulk adsorbents and thin film. The load applied were at a range of 300–5000 mN.

3 Results and Discussion

The optical images of the bulk-shaped adsorbents at pressure of 148 MPa using binderless compression are shown in Fig. 1. The fabricated bulk-shaped adsorbent diameter is at ca. 13 mm, the dimension of evacuable die set size.

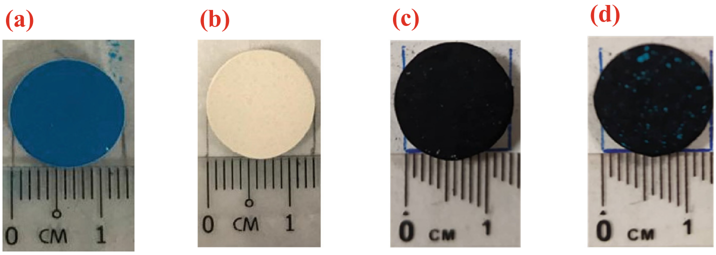

Fig. 1. Optical image of bulk-shaped adsorbents at pressure of 148 MPa.

The optical image in Fig. 2 shows Cu-MOF thin-film with different binder exhibited similar light blue colour. Thin film using gA showed a good adhesion property when the thin-film firmly hold on the soda-lime glass surface. Cu-MOF thin-film (gA) was observed with a shiny surface and smoothly covered on the glass surface. Cu-MOF thin-film (PVA) produced the same result Cu-MOF thin-film (gA). However, the surface was observed with a slightly bubble-like texture due to strong adhesion properties that effected the surface when the screen-printing mesh was removed. Thin-film using PODFA shows a dull and dusty surface with powdery residue due to low adhesion properties.

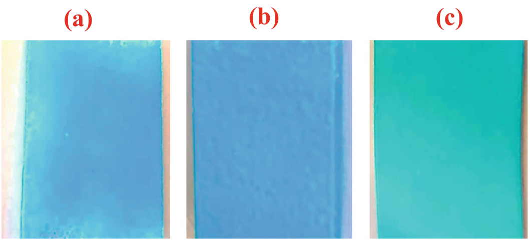

Fig. 2. Optical image of MOF-199 thin-film (a) gum Arabic, gA (b) polyvinyl acetate, PVA and (c) fatty alcohol, PODFA.

Figure 3 shows the XRD pattern of MOF-199 bulk adsorbents and thin film. There are nine prominent peaks assigned to (200), (220), (222), (422), (440), (442), (731), (751), and (773) for bulk and thin film [3–5]. The presence of (222) peak at 2θ = 11.7° suggested the successful retainment of crystalline phase of as-synthesized MOF-199 based on JCPDS index No. 01–1142 and No. 48–1548 [6]. However, bulk adsorbents exhibited reduced crystallinity where the structure of adsorbent when subjected to higher compression as reported [7]. Hybrid adsorbents exhibited similar peaks of pure MOF-199 suggesting successful binder-less compression with reduced crystallinity for prominent peaks.

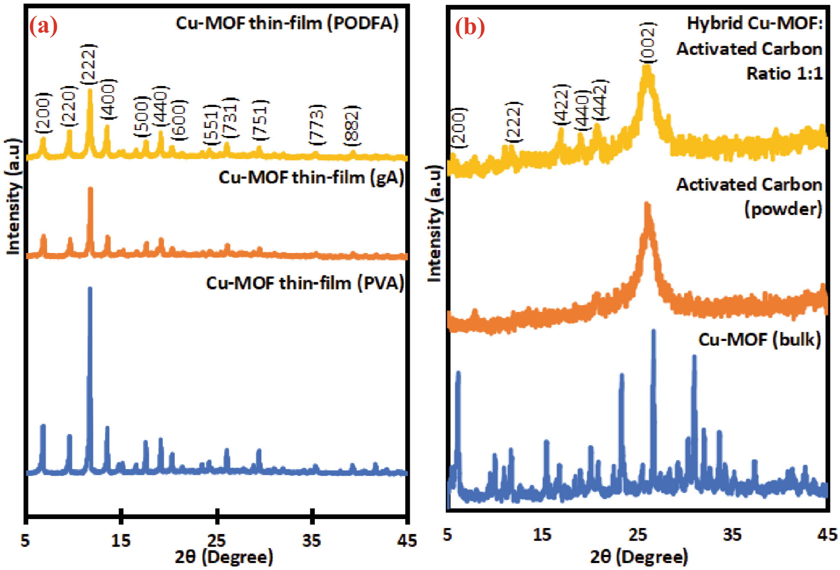

Fig. 3. XRD patterns of MOF-199 thin film and bulk adsorbents.

The highest peak of (222) was observed for PVA in corellation of their retained morphology observed in Fig. 4. The exhibited prominent peaks were similar as reported in previous study [8]. Figure 4 shows the morphology of MOF-199 thin-film prepared using screen-printing method gA, PVA and PODFA as binders. Morphology of all thin-film samples exhibited agglomerations and flaky particles except for thin film prepared using gA with a gel-like coated particle around the structure that improves overall surface structure. On the other hand, Fig. 5 shows the morphology of bulk-shaped adsorbents. MOF-199 bulk adsorbents exhibited agglomeration without well-defined octahedral structure. Zeolite 13X exhibited similar morphology of intergrown octahedral crystals as reported in previous studies [9]. Meanwhile, commercial AC exhibited string-likestructure [3]. Hybrid adsorbent was successfully formed due to the presence of crystalline structure and string-like structure that were seen lumped together suggesting that the morphology of hybrid adsorbent was not affected by binder-less compression.

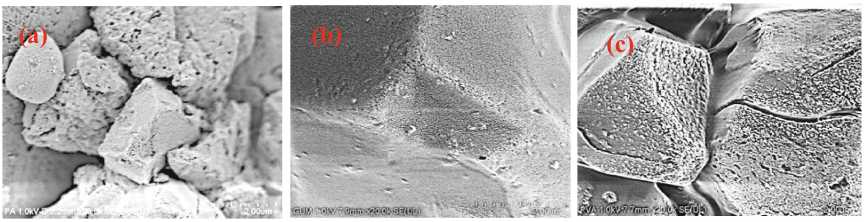

Fig. 4. FESEM image of thin film using (a) PODFA (b) gA and (c) PVA.

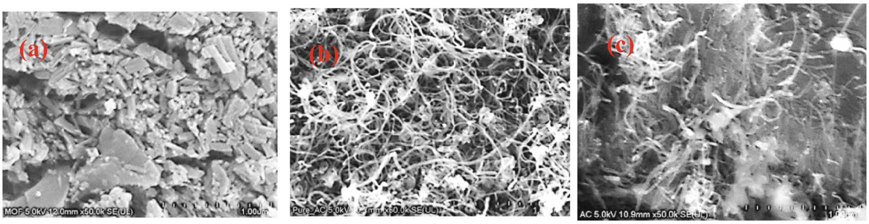

Fig. 5. FESEM images of bulk adsorbents (a) MOF-199 (b) Zeolite 13X (c) AC and (d) Hybrid MOF-199:AC (1:1).

Figure 6 shows the plot of reduced modulus, R*, (GPa) and hardness (GPa) curves against contact depth, hc (nm). The contact depth also increases as the load applied increases, and the logarithmic line was generated from the plotted point. The reduced modulus, R* (GPa) shows an increment as the contact depth was increased and the average reduced modulus. Average R* and hardness value of MOF-199 bulk adsorbents was lower than thin film. Reduced modulus (R*) for pure MOF-199 and hybrid MOF-199:AC bulk adsorbents were at ca. 2.818 GPa and 0.002 GPa, respectively suggesting that hybrid adsorbent was not suitable for applications due to lack of hardness.

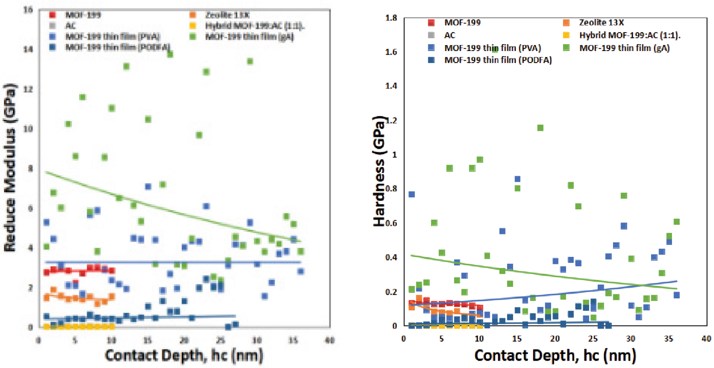

Fig. 6. Mechanical stability of (a) Reduced modulus and (b) Hardness of MOF-199.

Reduced modulus value of MOF-199 thin-film were higher at ca. 6.577 GPa (gA), 3.539 GPa (PVA), and 0.816 GPa (PODFA), respectively. The different occur due to the characteristic of the bulk shaped adsorbent and thin-film. The high value in both field for thin-film indicating a strong substrate attachment strength that form during the synthesis method. While for binderless compression method, the adsorbent has a porosity characteristic that affected their overall value. It was reported that the effect of pelletization revealed that at pressures of 0.07 GPa can induce partial pore collapse in MOF-199 structure [10].

4 Conclusion

The potential of MOF-199 synthesized using facile method to be further fabricated into bulk adsorbents and thin film to obtain usable macro structure for transition from powder to industrial applications were successfully demonstrated. It was found that binder-less compression method and screen printed thin film using various new binder materials resulted in highly mechanically stable macro-shaped structure.

Acknowledgement. The authors thank BOLD2025(10436494/B/2019101) and URND(UTG-RD-19–08).

References

1. Jiang, L., Gonzalez-Diaz, A., Ling-Chin, J., Roskilly, A.P., Smallbone, A.J.: Appl. Energy. **245**(1), 1–15 (2019)
2. Spigarelli, B.P., Kawatra, S.K.: Elsevier Ltd. **1**, 69–87 (2013)
3. Palisoc, S., Marco, J., Natividad, M.: Heliyon. **6**, e03202 (2020)
4. Zarghampoor, M.H., Mozaffarian, M., Chrisnardy, F., Krisnandi, Y.K.: Mater. Sci. Eng. 1–7 (2017)
5. Kaur, R., Kaur, A., Umar, A., Anderson, W.A., Kansal, S.K.: Mater. Res. Bull. **109**, 124–133 (2019)
6. Rashidi, N.A., Yusup, S.: Elsevier Ltd. **13**, 1–16 (2016)
7. Misran, H., Othman, S.Z., Manap, A., Pauzi, N.I.M., Ramesh, S.: Sci. Adv. Mater. **6**, 1638–1644 (2014)
8. Mahadi, N., et al.: Adv. Mat. Res. **1115**, 426–429 (2015)
9. Schumann, K., Unger, B., Brandt, A., Scheffler, F.: Microporous and Mesoporous Materials **154**, 119–123 (2012)
10. Redfern, L.R., Farha, O.K.: Chem. Sci. **10**, 10666–10679 (2019)