

Jianwei Ren<sup>a</sup>, Tshiamo Segakweng<sup>a</sup>, Henrietta W. Langmi<sup>a</sup>, Nicholas M. Musyoka<sup>a</sup>, Brian C. North<sup>a</sup>, Mkhulu Mathe<sup>a</sup>, Dmitri Bessarabov<sup>b</sup>

<sup>a</sup>HySA Infrastructure Centre of Competence, Materials Science and Manufacturing, Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa

<sup>b</sup>HySA Infrastructure Centre of Competence, Faculty of Engineering, North-West University (NWU), Potchefstroom, South Africa

# Microwave-assisted modulated synthesis of zirconium-based metal–organic framework (Zr-MOF) for hydrogen storage applications

Zirconium-based metal–organic framework (Zr-MOF) was synthesized using a microwave-assisted modulated method in a short reaction time of 5 min. The Zr-MOF material was highly crystalline with well-defined octahedral shaped crystals, and it exhibited comparable hydrogen storage capacity to Zr-MOF of similar specific surface area synthesized using conventional methods with much longer synthesis time.

**Keywords:** Zirconium-based metal–organic framework; Modulated synthesis; Microwave-assisted synthesis; Hydrogen storage

## 1. Introduction

Zirconium-based metal–organic framework (Zr-MOF) materials have recently attracted considerable interest due to their remarkable chemical and mechanical stabilities, which will facilitate their industrial application in areas such as catalysis [1], gas adsorption [2] and gas separation processes [3]. However, it is difficult to obtain Zr-MOF comprising a regular crystalline morphology by following the synthetic procedure reported by Cavka et al. [4], and instead irregular microcrystalline polyhedra of Zr-MOF are often obtained. In our initial attempts to synthesize Zr-MOF using the reported procedure we encountered some difficulties; either the Zr-MOF precipitated as micro-sized aggregates of nanocrystals, or disordered phases formed, which exhibited low specific surface area and low hydrogen adsorption capacity. However, following a modulated synthesis approach well-defined octahedral shaped Zr-MOF crystals of high reproducibility and with enhanced hydrogen storage capacity could be produced within a reaction time of 2 h [5, 6], and larger Zr-MOF crystals could be obtained with a prolonged reaction time [7]. Microwave heating typically enables short reaction times, and fast kinetics of crystal nucleation and growth, and has only recently been applied in the preparation of multi-dimensional coordination polymers although it has played a role in organic chemistry for several decades [8–10]. Liang et al. [10] reported microwave-assisted solvothermal synthesis

of zirconium oxide based MOFs, and obtained highly crystalline products that appeared as plate-like crystallites. The materials were not applied for hydrogen storage. Here we performed a microwave-assisted modulated synthesis of Zr-MOF (denoted as Zr-MOF-MW), in an attempt to obtain a product of high crystallinity with desirable properties for hydrogen storage applications, in a short synthesis time. The results were compared with those of Zr-MOF synthesized by conventional heating in an oven (denoted as Zr-MOF-Oven).

## 2. Experimental procedure

### 2.1. Reagents and chemicals

Zirconium tetrachloride (ZrCl<sub>4</sub>, Sigma-Aldrich, 99.5+ %), terephthalic acid (Sigma-Aldrich, 98 %), N,N-dimethylformamide (DMF, Sigma-Aldrich, 99.8 %), formic acid (HCOOH, Sigma-Aldrich, 95+ %) and anhydrous chloroform (Sigma-Aldrich, 99+ %) were purchased and used without further purification.

### 2.2. Modulated synthesis of Zr-MOF-Oven sample

The synthesis of Zr-MOFs was conducted using a 250 ml flat-bottom flask and a temperature controlled oven to provide constant reaction temperature. In a typical procedure, 0.75 g (4.5 mmol) terephthalic acid and 1.05 g (4.5 mmol) zirconium tetrachloride were ultrasonically dissolved in 40 ml DMF solvent. Then 17 ml (450 mmol) formic acid was added as a modulator. The flask was Teflon-sealed and placed in a pre-heated oven for 24 h at 120 °C under static conditions. After filtration, the obtained white product was ultrasonically washed with anhydrous chloroform for 30 min. Then the solid was re-collected and dried under vacuum at room temperature.

### 2.3. Microwave-assisted modulated synthesis of Zr-MOF-MW sample

The microwave-assisted synthesis of Zr-MOFs was conducted in a microwave reaction system (Anton Paar Synthos 3000). In a typical procedure, 0.75 g (4.5 mmol)

terephthalic acid and 1.05 g (4.5 mmol) zirconium tetrachloride were ultrasonically dissolved in 40 ml DMF solvent. Then 17 ml (450 mmol) formic acid was added and the starting solution was split into four portions. Four microwave vessels were programmed for reaction at 120 °C for 5 min under static conditions. After reaction, the sample was treated in the same manner as the Zr-MOF-Oven sample.

#### 2.4. Characterization

Powder X-ray diffraction (PXRD) patterns were obtained at room temperature by using a PANalytical X'Pert Pro powder diffractometer with Pixcel detector using Ni-filtered Cu-K $\alpha$  radiation (0.154 nm) in the range of  $2\theta = 1-90^\circ$ , and scanning rate of  $0.1^\circ \cdot \text{s}^{-1}$ . The exposure time of sample to environment was about 20 min including the sample preparation and testing procedure. An Auriga Cobra focused-ion beam scanning electron microscope (FIB-SEM) was used to study the morphology of the Zr-MOF samples. All the samples were mounted on carbon tape and coated with gold prior to measurement. Thermal stability of the obtained Zr-MOFs was evaluated using a thermogravimetric analysis (TGA) instrument (Mettler, Toledo, TGA/SDTA 851 $^\circ$ ). 10 mg of Zr-MOF sample was loaded into a pan and heated to 1000 °C at a rate of  $10 \text{ K} \cdot \text{min}^{-1}$ . The air gas flow was maintained at  $10 \text{ mL} \cdot \text{min}^{-1}$ .

Surface area and pore characteristic measurements were carried out on an ASAP 2020 HD analyzer (Micromeritics) using N $_2$ , and the BET surface areas were obtained from the linear region of the N $_2$  isotherms using the two consistency criteria suggested in the literature [11–13].

Volumetric H $_2$  adsorption isotherms at 77 K and up to 1 bar were also measured on the ASAP 2020 instrument. All

gas sorption isotherms were obtained using ultra-high purity grade (99.999%) gas. Before analysis, the pre-treated MOF samples (0.2–0.3 g) were outgassed in the analysis tube under vacuum (down to  $10^{-7}$  bar) with heating up to 200 °C, which is sufficient to remove solvent molecules without thermal decomposition or loss of framework crystallinity.

### 3. Results and discussion

Powder XRD patterns and the corresponding SEM images of the Zr-MOF-Oven and Zr-MOF-MW materials are shown in Fig. 1. The PXRD patterns of both samples showed the full set of sharp diffraction peaks belonging to Zr-MOF (also known as UiO-66) [4]. Similarly to other MOF materials, the relative intensities of the reflection peaks normally give qualitative information of the crystallinity [14]. The Zr-MOFs showed a high degree of crystallinity. It can be seen from the SEM image that the Zr-MOF crystals obtained from 24 h oven reaction undoubtedly were octahedral shaped with sharp edges and well-defined facets. The crystal sizes were in the range of 1–3  $\mu\text{m}$ . For the microwave reaction, not only was the same degree of crystallinity achieved within a much shorter reaction time of 5 min, but also clearly defined octahedral shaped crystals of sizes 0.5–3  $\mu\text{m}$  were obtained as shown in the SEM image. These results illustrate that the use of microwave significantly reduces the synthesis time of Zr-MOF without compromising the crystallinity of the material.

Weight loss profiles from thermogravimetric analysis (TGA) showed principally two stages in weight loss for both the as-prepared Zr-MOF-Oven and Zr-MOF-MW samples (Fig. 2). Generally, in the first stage the mass dropped almost steadily up to about 350 °C as the sample

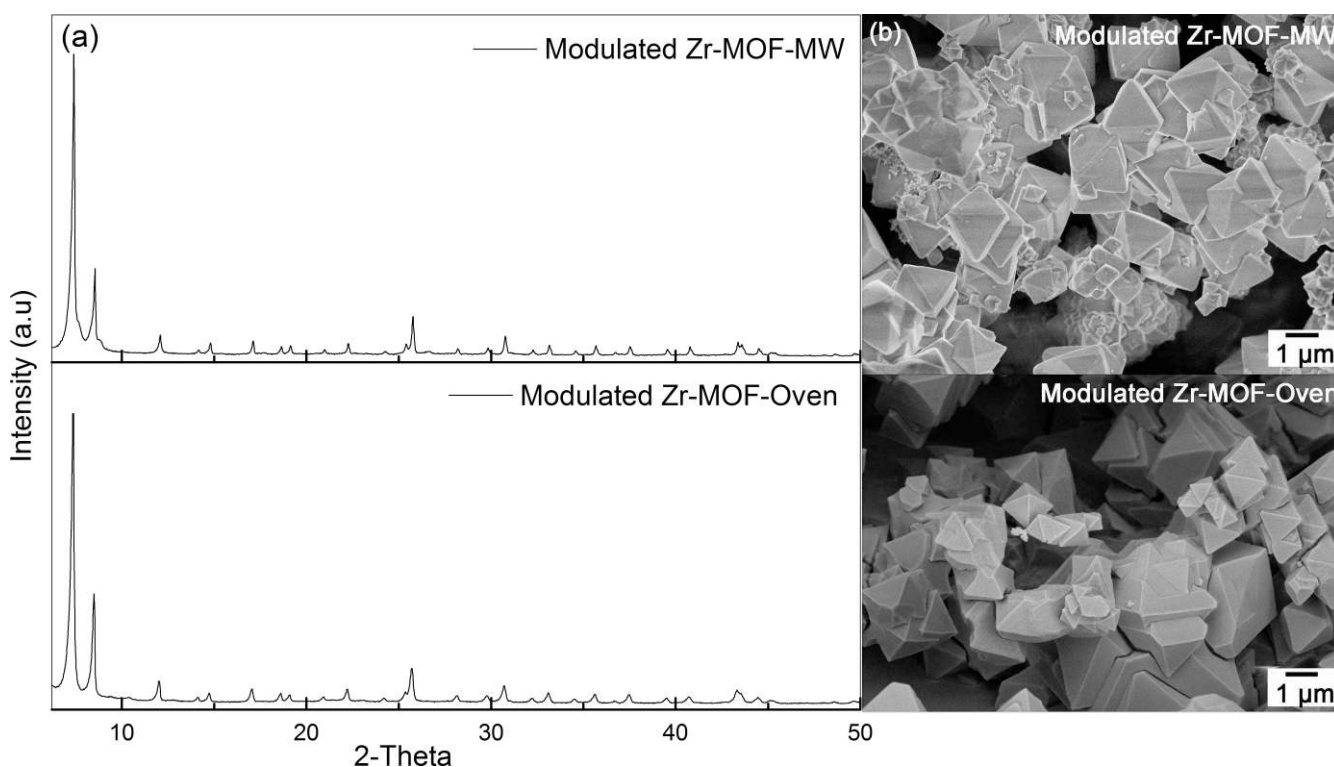


Fig. 1. (a) PXRD patterns and (b) SEM images of Zr-MOF-Oven and Zr-MOF-MW samples.

was heated. This mass loss was most likely associated with the removal of all organic materials, including the evaporation of guest molecules such as solvent DMF and chloroform from the pores. The modulated Zr-MOF-MW sample showed less weight loss, indicating that it contained less guest organic materials. Between 350 and 500 °C a nearly constant weight was recorded as the weight loss curve was almost flat indicating that the Zr-MOFs had high thermal stabilities. The TGA profile of the Zr-MOF-Oven sample was in close agreement with that of UiO-66 originally reported by Cavka et al. [4]. Above 500 °C the mass dropped abruptly, implying that both Zr-MOFs retained their structure up to 500 °C and above this temperature the materials decomposed to form  $\text{ZrO}_2$ . These TGA results demonstrate that microwave-assisted synthesis also produces highly crystalline Zr-MOFs with high thermal stability.

The nitrogen adsorption isotherms at 77 K of desolvated Zr-MOF-Oven and Zr-MOF-MW powder samples were Type I in nature (Fig. 3a), characteristic of a structure with micropores [15]. The textural properties and hydrogen uptake capacities of the desolvated Zr-MOF-Oven and Zr-MOF-MW samples are given in Table 1, alongside reported values in the literature. The Langmuir surface areas (not shown in the table) determined from the sorption isotherms were 1581 and 1186  $\text{m}^2 \cdot \text{g}^{-1}$  for Zr-MOF-Oven and Zr-MOF-MW, respectively. The latter value is very similar to the reported value of 1187  $\text{m}^2 \cdot \text{g}^{-1}$  for UiO-66 [16]. The BET surface areas and total pore volumes were 1367  $\text{m}^2 \cdot \text{g}^{-1}$  and 0.56  $\text{cm}^3 \cdot \text{g}^{-1}$ , respectively for Zr-MOF-Oven, and 1087  $\text{m}^2 \cdot \text{g}^{-1}$  and 0.44  $\text{cm}^3 \cdot \text{g}^{-1}$ , respectively for Zr-MOF-MW. The difference in surface areas between the Zr-MOF-Oven and Zr-MOF-MW samples also complements the observed differences in weight loss curves shown in Fig. 2. The BET surface areas obtained here are within range of those reported for various UiO-66 samples shown in Table 1. The inserted Horvath–Kawazoe differential pore volume plots exhibited two main regions of pores at 7.8 and 11.3 Å along side others for Zr-MOF-Oven sample. While for Zr-MOF-MW sample, only one region of pores at 11 Å was observed. The absence of pores around 8 Å for the Zr-MOF-MW sample may, at least in part, be responsible for the lower surface area and pore volume when com-

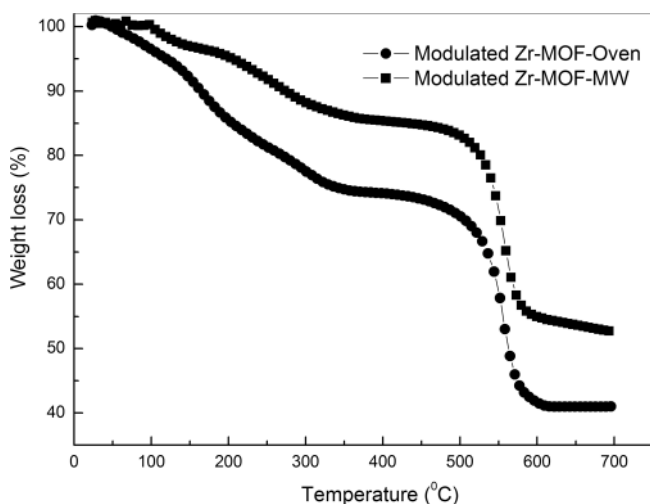


Fig. 2. Thermogravimetric analysis of the as-prepared Zr-MOF-Oven and Zr-MOF-MW samples.

pared to the Zr-MOF-Oven sample. The  $\text{H}_2$  adsorption isotherms for the desolvated Zr-MOF-Oven and Zr-MOF-MW samples are presented in Fig. 3b. At 77 K and approximately 1 bar, the hydrogen storage capacity reached 1.5 wt.% for Zr-MOF-Oven, which is among the high values reported in the literature (see Table 1). Meanwhile under the same conditions a hydrogen storage capacity of 1.26 wt.% was attained for Zr-MOF-MW, in agreement with the lower values from the literature for UiO-66 (see Table 1). The higher hydrogen storage capacity for Zr-MOF-Oven sample may be benefitted by the multiple regions of pore size distributions. At 77 K and approximately 1 bar a direct relationship between hydrogen storage capacity and the specific surface area of materials exists [17]. The hydrogen storage capacities obtained in this work correlated very well with the BET surface areas of the Zr-MOFs. These results demonstrate that although the microwave-assisted modulated synthesis method generates Zr-MOF with relatively lower specific surface area, pore volume and hydrogen storage capacity than those of the Zr-MOF produced by conventional heating in an oven, these properties of the former are comparable to some literature

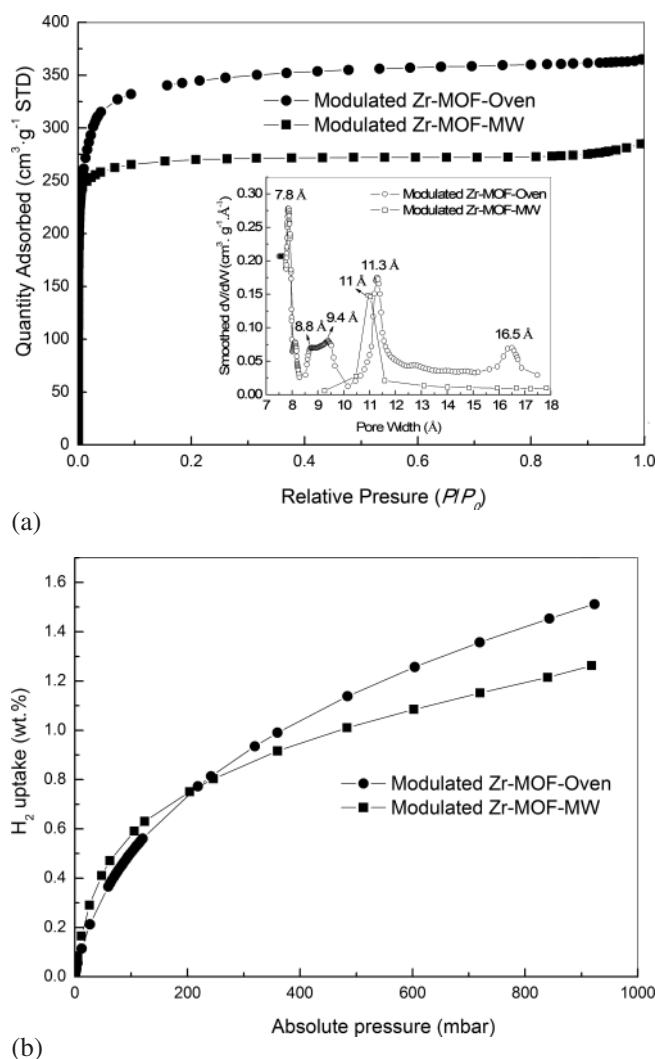


Fig. 3. (a)  $\text{N}_2$  sorption isotherms (insert, Horvath–Kawazoe differential pore volume plot), and (b)  $\text{H}_2$  sorption isotherms at 77 K and 1 bar for the desolvated Zr-MOF-Oven and Zr-MOF-MW samples.



Table 1. Comparison of physical properties and H<sub>2</sub> uptake capacities of the Zr-MOF samples reported in the literatures and prepared in this work.

Sample	Size <sup>a</sup>	Synthesis	S <sub>BET</sub> (m <sup>2</sup> · g <sup>-1</sup> ) <sup>b</sup>	Pore vol. (cm <sup>3</sup> · g <sup>-1</sup> ) <sup>c</sup>	Micropore vol. (cm <sup>3</sup> · g <sup>-1</sup> ) <sup>d</sup>	H <sub>2</sub> uptake (wt.%) <sup>e</sup>	Ref.
UiO-66	200 nm	Solvothermal	1080	–	–	1.28	[4]
UiO-66	100–200 nm	Solvothermal	1020	–	–	1.24	[18]
UiO-66	100 nm	Solvothermal	1434	0.65	0.43	1.6	[19]
UiO-66	150–200 nm	Solvothermal	1358	–	–	1.49	[20]
Zr-MOF-Oven	1–3 μm	Modulated solvothermal	1367	0.56	0.44	1.5	This work
Zr-MOF-MW	0.5–3 μm	Modulated microwave	1087	0.44	0.38	1.26	This work

<sup>a</sup>Estimated from SEM images. <sup>b</sup>BET surface area. <sup>c</sup>From H-K analysis. <sup>d</sup>From H-K analysis. <sup>e</sup>Adsorbed at 77 K and approximately 1 bar.

values [4, 18–20], with the Zr-MOF-MW displaying superiority in terms of crystal size and morphology, and the added advantage of extremely short synthesis time for this material.

#### 4. Conclusions

In summary, the employment of a microwave-assisted modulated method in the synthesis of Zr-MOF yields a high quality crystalline material with significant hydrogen storage capacity within a very short reaction time. Such an approach would facilitate production of the material on an industrial scale for hydrogen storage applications.

The authors would like to acknowledge the financial support from the South African Department of Science and Technology (DST).

#### References

- [1] C.G. Silva, I. Luz, I. Llabrés, F.X. Xamena, A. Corma, H. García: *Chem. Eur. J.* 16 (2010) 11133. DOI:10.1002/chem.200903526
- [2] H. Wu, Y.S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim, W. Zhou: *J. Am. Chem. Soc.* 135 (2013) 10525. DOI:10.1021/ja404514r
- [3] Q.Y. Yang, A.D. Wiersum, P.L. Llewellyn, V. Guillerm, C. Serre, G. Maurin: *Chem. Commun.* 47 (2011) 9603. DOI:10.1039/C1CC13543K
- [4] J.H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K.P. Lillerud: *J. Am. Chem. Soc.* 130 (2008) 13850. DOI:10.1021/ja8057953
- [5] T. Tsuruoka, S. Furukawa, Y. Takashima, K. Yoshida, S. Isoda, S. Kitagawa: *Angew. Chem. Int. Ed.* 48 (2009) 4739. DOI:10.1002/anie.200901177
- [6] F. Vermoortele, B. Bueken, G.L. Bars, B. Van de Voorde, M. Vandichel, K. Houthoofd, A. Vimont, M. Daturi, M. Waroquier, V. Van Speybroeck, C. Kirschhock, D.E. De Vos: *J. Am. Chem. Soc.* 135 (2013) 11465. DOI:10.1021/ja405078u
- [7] J.W. Ren, H.W. Langmi, B.C. North, M. Mathe, D. Bessarabov: *Int. J. Hydrogen Energy* 39 (2014) 890. DOI:10.1016/j.ijhydene.2013.10.087
- [8] J. Klinowski, F.A. Almeida, P. Paz, Silva, J. Rocha: *Dalton Trans.* 40 (2011) 321. DOI:10.1039/C0DT00708K
- [9] J.Y. Choi, J. Kim, S.H. Jung, H.K. Kim, J.S. Chang, H.K. Chae: *Bull. Korean Chem. Soc.* 27 (2006) 1523. DOI:10.5012/bkcs.2006.27.10.1523
- [10] W.B. Liang, D.M. D'Álessandro: *Chem. Commun.* 49 (2013) 3706. DOI:10.1039/C3CC40368H

- [11] K.S. Walton, R.Q. Snurr: *J. Am. Chem. Soc.* 129 (2007) 8552. DOI:10.1021/ja071174k
- [12] Q. Zhao, W. Yuan, J.M. Liang, J.P. Li: *Int. J. Hydrogen Energy* 38 (2013) 13104. DOI:10.1016/j.ijhydene.2013.01.163
- [13] H.R. Abid, H.Y. Tian, H.M. Ang, M.O. Ang, M.O. Tade, C.E. Buckley, X.B. Wang: *Chem. Eng. J.* 187 (2012) 415. DOI:10.1016/j.cej.2012.01.104
- [14] J. Hafizovic, M. Bjørgen, U. Olsbye, P.D.C. Dietzel, S. Bordiga, C. Prestipino, C. Lamberti, K.P. Lillerud: *J. Am. Chem. Soc.* 129 (2007) 3612. DOI:10.1021/ja0675447
- [15] H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi: *Nature* 402 (1999) 276. DOI:10.1038/46248
- [16] P.S. Barcia, D. Guimaraes, P.A.P. Mendes, J.A.C. Silva, V. Guillerme, H. Chevreau, C. Serre, A.E. Rodrigues: *Micro. Meso. Mater.* 139 (2011) 67. DOI:10.1016/j.micromeso.2010.10.019
- [17] B.D. Adams, C.K. Ostrom, S. Chen, A.C. Chen: *J. Phys. Chem. C* 114 (2010) 19875. DOI:10.1021/jp1085312
- [18] J. Hafizovic, U. Olsbye, K.P. Lillerud, S. Jacobsen, N. Guillou: *Metal organic framework compounds*. US 2012/0115961 A1, May 10, 2012.
- [19] J. Rouquerol, P. Llewellyn, F. Rouquerol: *Stud. Surf. Sci. Catal.* 160 (2007) 49. DOI:10.1016/S0167-2991(07)80008-5
- [20] Y.S. Bae, A.Ö. Yazaydn, R.Q. Snurr: *Langmuir* 26 (2010) 5475. DOI:10.1021/la100449z

(Received October 29, 2013; accepted January 20, 2014)

#### Bibliography

DOI 10.3139/146.111047  
*Int. J. Mater. Res. (formerly Z. Metallkd.)*  
 105 (2014) E; page 1–4  
 © Carl Hanser Verlag GmbH & Co. KG  
 ISSN 1862-5282

#### Correspondence address

Dr. Jianwei Ren  
 HySA Infrastructure Centre of Competence  
 Materials Science and Manufacturing  
 Council for Scientific and Industrial Research (CSIR)  
 PO Box 395, Pretoria 0001  
 South Africa  
 Tel.: +27 128412967  
 Fax: +27 128412135  
 E-mail: JRen@csir.co.za