Journal Name

ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Room temperature synthesis of Cu-BTC coordination polymer and metal-organic framework by pH control[†]

Shiraz Ahmed Siddiqui,[a] Alexander Prado-Roller,[b] and Hidetsugu Shiozawa[*a,c]

Received Date
Accepted Date

DOI: 00.0000/xxxxxxxxxx

Synthesis of crystalline materials is crucial in the field of coordination chemistry. In the present work, the reaction between the copper and benzene-1,3,5-tricarboxylic acid (BTC) ligand is controlled by adjusting the pH of the reaction mixture to synthesize two crystalline structures: metal-organic framework HKUST-1 and one-dimensional coordination polymer Cu(BTC)·3H_2O. Single crystals of both structures are studied by multi-laser Raman spectroscopy. It is found that both crystals exhibit photoluminescence. Also, the transformation of HKUST-1 into Cu(BTC)·3H_2O is demonstrated. This work provides impetus for researchers to synthesize large metal-organic crystals.

Coordination compounds consists of a metal atoms/ions (Lewis acid) bonded by an organic ligand (Lewis base) with a coordinate covalent bond[1 2–4]. The unique, diverse properties of coordination compounds has proved beneficial for the developments in field of electronics, sensors, magnetism and medical research. Coordination polymers are solid-state structures consisting of repeating coordination units to form 1D extended chains, 2D sheets or 3D frameworks[5 6–8]. Coordination polymers having a porous structure is known as metal-organic frameworks (MOFs)[9–11],[12],[13],[14],[15 16] Synthesizing large and quality crystals of MOFs benefits in a wide range of applications. Porosity together with large size offers potential in separation, heterogeneous catalysis[17],[18],[19], gas-sorption[20],[21], chromatography[22,23], optoelectronics, magnetism and sensing applications[24],[25].

Controlling the process of crystallisation by pH control is a challenging, yet fascinating process in understanding the chemistry of materials[26–28]. The pH modulating technique was previously utilized to synthesize MOFs[29],[30],[31],[32],[33],[34],

In the present work, the reaction between copper and benzene-1,3,5-tricarboxylic (BTC) acid is controlled by adjusting the pH of the reaction mixture to obtain crystals of two different coordination compounds- $Cu_3(BTC)_2(H_2O)_3$ (also known as HKUST-1[35] or MOF-199) and Cu(BTC)·3H_2O where BTC= benzene-1,3,5-tricarboxylic acid (see Figure 1).

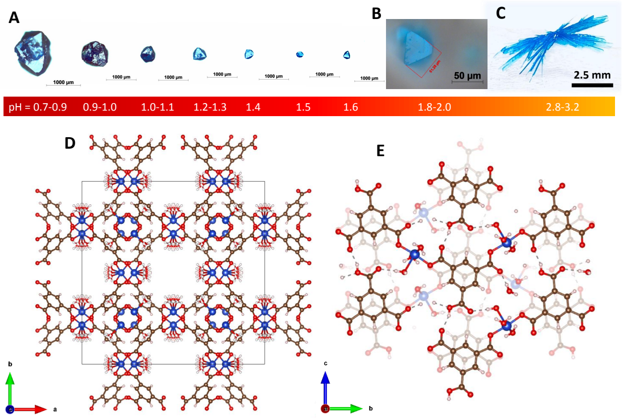

Fig. 1 (A) pH-dependent crystallisation of HKUST-1 (strong acid conditions-using HNO_3). (B) Synthesis of HKUST-1 crystal without any pH adjustment (as-synthesized). (C) pH-dependent crystallisation of Cu(BTC)·3H_2O, weak acid conditions using deionised water. (A-B) Crystallographic representation of HKUST-1 Cu(II) paddlewheel structure (C) Cu(BTC)·3H_2O 1D coordination polymer view along [100] crystallographic plane.

Most of the literature reports the synthesis of HKUST-1 using hydrothermal/solvothermal method. The high-temperature synthesis yields crystals suitable for x-ray diffraction (XRD) measurements, but the problem is that a significant amount of Cu_2O is obtained as by-product. This by-product remains in the pores of

---

[a] *Faculty of Physics, University of Vienna, Boltzmanngasse 5, Vienna, Austria. Fax:+43-1-4277-9726; Tel:+43-1-4277-72601; E-mail: hidetsugu.shiozawa@univie.ac.at*

[b] *Department of Inorganic Chemistry, University of Vienna, Währinger Straße 42, 1090, Vienna, Austria*

[c] *J. Heyrovsky Institute of Physical Chemistry, Czech Academy of Sciences,Dolejskova 3,Prague, Czech Republic.*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 00.0000/00000000.

‡ Additional footnotes to the title and authors can be included *e.g.* 'Present address:' or 'These authors contributed equally to this work' as above using the symbols: ‡, §, and ¶. Please place the appropriate symbol next to the author's name and include a `\footnotetext` entry in the the correct place in the list.

the framework and reduces the specific surface area thereby causing hinderance in gas absorption application[36]. Thus, room temperature synthesis of HKUST-1 is beneficial. Our pH controlled synthesis procedure will help the community to synthesize quality and large crystals of HKUST-1 at room temperature.

Copper (II) based coordination polymers are one of the most studied compounds in the field of natural science and medical research. Owing to the magnificent antibacterial activity, low toxicity and potential as biomaterials, these compounds are gaining interest among researchers[37]. Large and quality crystals of Cu(BTC)$\cdot$3H_2O is synthesized at room temperature by obtaining weak acid conditions i.e. pH greater than 2.1. Single crystal x-ray diffraction (SXRD) shows that the structure is composed of 1D zig-zag chains interconnected by hydrogen bonding which makes the structure stable and generates a 3D coordination network[38] .

Finally, the knowledge acquired through this pH dependent synthesis route helps us transform the porous HKUST-1 framework into Cu(BTC)$\cdot$3H_2O. This strategy is particularly useful as MOFs have porous structure capable of absorbing harmful gases and when MOFs decompose, these harmful gases are a threat to environment. Our technique to use deionised water is efficient and economical method in destroying the framework and transforming it into the non-porous Cu(BTC)$\cdot$3H_2O.

All the synthesis procedure demonstrated in this work is done at room temperature. It is found that large crystals of HKUST-1 are synthesized by adjusting the pH of the reaction mixture in the pH range 0.7-1.6 shown in Figure 1A whereas crystals of Cu(BTC)$\cdot$3H_2O are synthesized in the pH range 2.2-3.2 shown in Figure 2B, C and D.

First, we present room temperature synthesis of HKUST-1 (crystal size 50-55 micrometers) without any pH adjustment.

Copper nitrate trihydrate $CuNO_3\cdot 3H_2O$ (1 mmol) and BTC (1 mmol) is dissolved in a mixture of three solvents (deionised water, DMF and ethanol), in the volummetric ratio 1:1:1 (pH=1.8-2.2). After 16-20 hours, crystals of HKUST-1 are formed at the bottom of the vial (pH=2.1-2.3). A clear depiction of the morphology of the as-synthesized HKUST-1 is shown in Figure 1B and bulk quality crystals showing the homogeneity is shown in Figure S1 in Supplementary information (SI)

The crystal obtained is measured by SXRD which confirms the well-known structure of HKUST-1 MOF Figure 1A-B. For detailed structure description refer to SI.

In order to obtain large and quality crystals of HKUST-1, our pH adjustment technique is useful. A stepwise decrease in pH of the reaction mixture by varying concentration of acid shows that large crystals in the millimeter range are synthesized in the pH range 0.7-0.9. This is done by adding 0.1 ml of strong acid i.e. nitric acid (HNO_3) in the reaction mixture. The resulting pH is in the range 0.7-0.9. After 8-10 days, large crystals of HKUST-1, crystal size ∼1-1.2 mm as shown in Figure 1 A is obtained. Large and bulk quality crystals are shown in Figure S2 in SI.

We also synthesized large crystals of HKUST-1 in the range ∼0.9-1.0 mm using 37% hydrochloric acid (HCl) instead of HNO_3 and copper chloride(CuCl) instead of $CuNO_3\cdot 3H_2O$. The morphology and crystal size is shown in Figure S3 in SI

The weak acid pH-condition (pH range 2.2-3.2) is favourable for obtaining crystals of Cu(BTC)$\cdot$3H_2O. Large crystals as shown in Figure 1C is obtained in the pH range 2.8-3.2 in 2-3 weeks after mixing the precursors.

The synthesis is done keeping the molar ratio of the two precursors 1:1 and the ratio of three solvents (deionised water, DMF, and ethanol) is 5:1:1. At this condition, the pH of the resulting reaction mixture is 2.1. After 3-4 hours, tiny-needle like feature appears as shown in Figure 2A. This indicates the point of nucleation. A stepwise increment in the pH value shows that as the pH increases, crystallisation is more evident. In the pH range 2.2-2.7, both tiny needles and bar shaped crystals are present as shown in Figure 2B and C. The quanity and quality of the crystals is improved when the pH is greater than 2.5. Also, when the pH is greater than 2.7 homogeneous crystals of bar shaped morphology as shown in Figure 2D is obtained without any tiny needle-like feature.

Crystallisation for tiny needles, shown in Figure 2A without any further pH adjustment takes approximately 4 weeks. In the pH range 2.2-2.4 (Figure 2B), crystallisation takes place in 12-16 hours whereas beyond 2.5 Figure 2C and D, crystals appear in 18-24 hours.

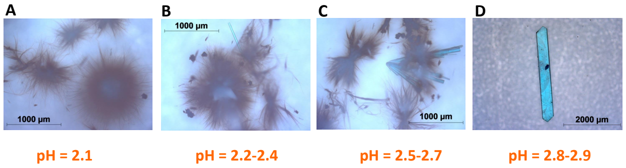

Fig. 2 A stepwise pH controlled synthesis of large crystals of Cu(BTC)$\cdot$3H_2O

The crystallinity of the obtained single crystal of Cu(BTC)$\cdot$3H_2O is examined by SXRD technique. The crystallographic representations of Cu(BTC)$\cdot$3H_2O packing structure along [100], [001] and [010] crystallographic plane are shown in Figure 3 A, B and C respectively .

The crystal structure is monoclinic with space group P21/n and lattice parameters a=6.7654, b=18.8135, c=8.5144; $\alpha = \gamma = 90^\circ$, $\beta = 92.439^\circ$. The empirical formula of the structure is $C_9H_{10}CuO_9$. The structure was previously reported in[37–41]. The metal ion copper is coordinated to the organic ligand BTC in the ratio (BTC:Cu= 1:1). The copper atom has square pyramidal coordination environment[41].

Figure 3 shows the 2D layers of the coordination polymer showing the hydrogen bonding (dotted line). The layers are held together by a combination of hydrogen bonding and π-π stacking of the BTC ligand. The distance between the planes of the offset aromatic ring is 3.435 angstrom.

BTC consists of three carboxylic acid group attached to the benzene ring. Two of three carboxylic group of the ligand is coordinated to the metal ion and thus forms a zig-zag polymeric chain. The third uncoordinated carboxylic group together with the coordinated water molecules make the hydrogen bonding between the chains. The three water molecules are coordinated to the copper which has the distorted square pyramidal or pentacoordinate geometry (Jahn-Teller distortation)[38].

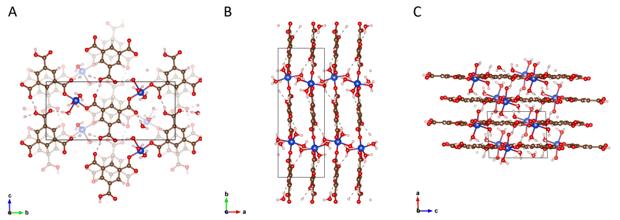

Fig. 3 Panels A, B and C shows the structures of $Cu(BTC){\cdot}3H_2O$ coordination polymer along the [100], [001] and [010] crystallographic planes, respectively.

Figure 4A shows the Raman spectra for HKUST-1 and $Cu(BTC){\cdot}3H_2O$ excited with a green laser ($\lambda = 514.5$ nm) focused on the single crystal as shown in Figure 4B and C. For HKUST-1, the bands appearing in the low frequency region i.e. below 600 cm^{-1} is due to the copper ions in the framework. The doublet at 177.54 cm^{-1} and 197.63 $^{-1}$ indicates that the MOF is hydrated and correspondingly Cu-Cu stretching modes appear[42,43]. The complex band at 275.49 cm^{-1} is indicative of the Cu-O_w stretching vibration, where O_w represents the oxygen of the water molecule adsorbed on Cu2+ ions.

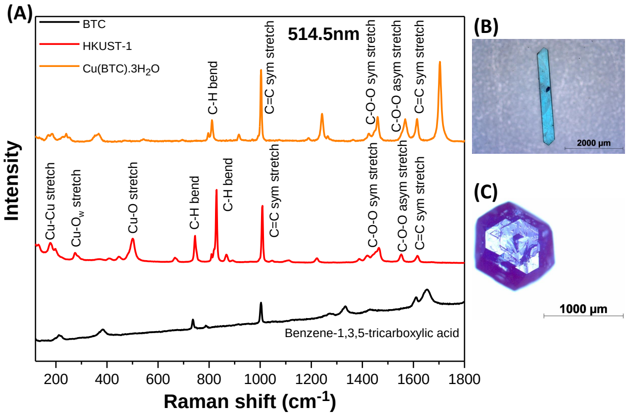

Fig. 4 Raman spectra of the HKUST-1 and $Cu(BTC){\cdot}3H_2O$ measured at λ = 514.5 nm. Panel B and C shows the single crystal of HKUST-1 and $Cu(BTC){\cdot}3H_2O$, respectively, on which the laser is focused.

The bands in the range 700-1800 cm^{-1} are mostly due to vibrational modes of the BTC ligand. The characteristic of C=C modes of benzene ring is found at 1008.87 and 1615.42 cm^{-1} for HKUST-1[42–45] whereas 1003.47 and 1614.44 cm^{-1} for $Cu(BTC){\cdot}3H_2O$.

In the HKUST-1 spectrum, the peaks at 745.15 and 829.29 cm^{-1} are designated as C-H bending vibrations[42,43]. The peak at 811.13 cm^{-1} is designated as C-H bending in case of $Cu(BTC){\cdot}3H_2O$. The peaks due to C-O-O symmetric and C-O-O asymmetric units are centered at 1464.72 and 1552.63 cm^{-1} for HKUST-1[46], and at 1459.81 and 1567.92 cm^{-1} for $Cu(BTC){\cdot}3H_2O$.

The analysis is consistent with the literature reports[42,46], [43,47], [44,45], [48].

The presence of luminescence for HKUST-1 and $Cu(BTC){\cdot}3H_2O$ crystals were examined using seven different excitation laser energies. The photoluminescence spectra of HKUST-1 and $Cu(BTC){\cdot}3H_2O$ crystal is shown in Figure 5 and Figure 6, respectively.

For HKUST-1, the luminescence peak appears in the range 770-970 nm with 633 nm laser and with 647 nm laser it appears in the range 720-940 nm.

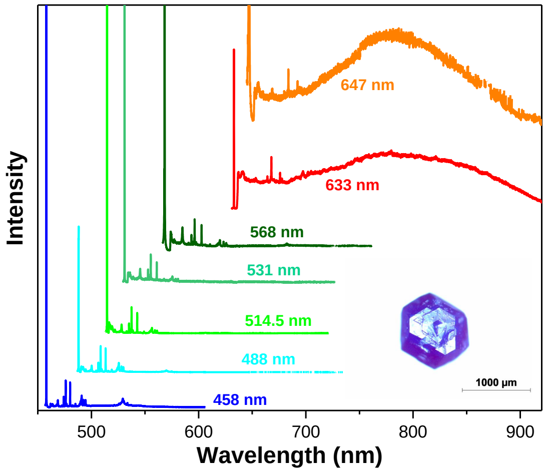

Fig. 5 Photoluminescence spectra of HKUST-1 crystal on the same spot measured using different lasers λ = 458, 488, 514.5, 531, 568, 633 and 647 nm, plotted on absolute wavelength scale. The inset shows the measured HKUST-1 crystal synthesized at pH=0.9

Similarly, for $Cu(BTC){\cdot}3H_2O$ the spectra recorded with laser wavelengths 488 nm, 514.5 nm, 531 nm, 568 nm and 633 nm have no luminescence whereas that recorded with 458 and 647 nm manifests a steadily increasing luminescence peak appearing at approximately 510-570 nm (in case of 458 nm) and 700-970 nm (for 647 nm).

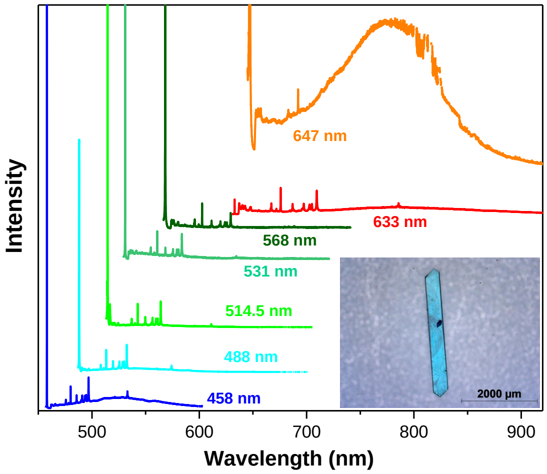

Fig. 6 Photoluminescence spectra of $Cu(BTC){\cdot}3H_2O$ on the same crystal spot measured using different lasers λ = 458, 488, 514.5, 531, 568, 633 and 647 nm, plotted on absolute wavelength scale. The inset shows the measured $Cu(BTC){\cdot}3H_2O$ crystal synthesized at pH=2.9

One of the major concern in the MOF research is that owing to the porosity the framework can absorb harmful gases. These harmful gases gets trapped in the pores of the framework and can cause a threat to environment. Our pH controlled analysis shows that by adjusting the pH of the reaction mixture the porous framework can be converted to non-porous Cu(BTC)$\cdot$3H_2O.

Our procedure is to extract a large crystal of HKUST-1 and immerse it in deionised water in such a way that the pH of the reaction mixture is in the range 2.8-3.2. The water molecule coordinates the metal site of the framework which results in increased coordination around the metal site. As a result, hydrolysis takes place and the organic ligand (BTC) is displaced away-destroying the framework. Ultimately, the metal hydroxide remains along with the protonated linker[41]. The pH range 2.8-3.2 is suitable for obtaining quality crystals of Cu(BTC)$\cdot$3H_2O (see Figure 2D) as discussed before. Furthermore, a detailed step by step procedure of slow conversion of as-synthesized HKUST-1 crystals into Cu(BTC)$\cdot$3H_2O without any pH adjustment is demonstrated in SI.

To conclude, the present work is focused on synthesis of quality crystals of two different chemical compounds i.e. metal organic framework HKUST-1 and coordination polymer Cu(BTC)$\cdot$3H_2O. We have demonstrated a room temperature, pH dependent synthetic route for obtaining large single crystals. HKUST-1 crystals can be synthesized in the millimeter range by adjusting the pH in the range 0.7-0.9, whereas quality crystals of Cu(BTC)$\cdot$3H_2O are synthesized in the pH range 2.8-3.2. HKUST-1 exhibits luminescence with red lasers λ = 633 and 647 nm while Cu(BTC)$\cdot$3H_2O shows luminescence with λ= 458 and 647 nm. The work is useful for researchers working in the field of MOFs and coordination polymers to synthesize large and quality crystals.

Notes and references

1 T. Damhus, R. Hartshorn, A. Hutton and N. Connelly, *Chemistry International – Newsmagazine for IUPAC*, 2005, **27**, 25–26.
2 M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *ACCOUNTS OF CHEMICAL RESEARCH*, 2008, **41**, 1782–1789.
3 S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Ohrstrom, M. O'Keeffe, M. P. Suh and J. Reedijk, *CRYSTENGCOMM*, 2012, **14**, 3001–3004.
4 R. R. Crichton, *Biological Inorganic Chemistry (Second Edition)*, Elsevier, Oxford, Second Edition edn, 2012, pp. 21–34.
5 S. Batten, S. Neville and D. Turner, *COORDINATION POLYMERS: DESIGN, ANALYSIS AND APPLICATION*, ROYAL SOC CHEMISTRY, THOMAS GRAHAM HOUSE, SCIENCE PARK, CAMBRIDGE CB4 4WF, CAMBS, ENGLAND, 2009, pp. 1–424.
6 S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Ohrstrom, M. O'Keeffe, M. P. Suh and J. Reedijk, *PURE AND APPLIED CHEMISTRY*, 2013, **85**, 1715–1724.
7 L. Ohrstrom, *CRYSTALS*, 2015, **5**, 154–162.
8 E. R. Engel and J. L. Scott, *GREEN CHEMISTRY*, 2020, **22**, 3693–3715.
9 J. Rowsell and O. Yaghi, *MICROPOROUS AND MESOPOROUS MATERIALS*, 2004, **73**, 3–14.
10 J. R. Long and O. M. Yaghi, *CHEMICAL SOCIETY REVIEWS*, 2009, **38**, 1213–1214.
11 K. Biradha, A. Ramana and J. J. Vittal, *CRYSTAL GROWTH & DESIGN*, 2009, **9**, 2969–2970.
12 H. Li, M. Eddaoudi, M. O'Keeffe and O. Yaghi, *NATURE*, 1999, **402**, 276–279.
13 A. K. Cheetham and C. N. R. Rao, *SCIENCE*, 2007, **318**, 58–59.
14 C. Janiak and J. K. Vieth, *NEW JOURNAL OF CHEMISTRY*, 2010, **34**, 2366–2388.
15 Z.-G. Gu, D.-J. Li, C. Zheng, Y. Kang, C. Woell and J. Zhang, *ANGEWANDTE CHEMIE-INTERNATIONAL EDITION*, 2017, **56**, 6853–6858.
16 Z.-G. Gu and J. Zhang, *COORDINATION CHEMISTRY REVIEWS*, 2019, **378**, 513–532.
17 A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *CHEMICAL COMMUNICATIONS*, 2012, **48**, 11275–11288.
18 A. Corma, H. Garcia and F. X. L. I. Llabres i Xamena, *CHEMICAL REVIEWS*, 2010, **110**, 4606–4655.
19 Y. Wen, J. Zhang, Q. Xu, X.-T. Wu and Q.-L. Zhu, *COORDINATION CHEMISTRY REVIEWS*, 2018, **376**, 248–276.
20 R. Babarao, J. Jiang and S. I. Sandler, *LANGMUIR*, 2009, **25**, 5239–5247.
21 O. Zybaylo, O. Shekhah, H. Wang, M. Tafipolsky, R. Schmid, D. Johannsmann and C. Woell, *PHYSICAL CHEMISTRY CHEMICAL PHYSICS*, 2010, **12**, 8092–8097.
22 S. Han, Y. Wei, C. Valente, I. Lagzi, J. J. Gassensmith, A. Coskun, J. F. Stoddart and B. A. Grzybowski, *JOURNAL OF THE AMERICAN CHEMICAL SOCIETY*, 2010, **132**, 16358–16361.
23 L. Li, F. Sun, J. Jia, T. Borjigin and G. Zhu, *CRYSTENGCOMM*, 2013, **15**, 4094–4098.
24 J. W. Brown, B. L. Henderson, M. D. Kiesz, A. C. Whalley, W. Morris, S. Grunder, H. Deng, H. Furukawa, J. I. Zink, J. F. Stoddart and O. M. Yaghi, *CHEMICAL SCIENCE*, 2013, **4**, 2858–2864.
25 J. A. Mason, M. Veenstra and J. R. Long, *CHEMICAL SCIENCE*, 2014, **5**, 32–51.
26 N. D. Burrows, C. R. H. Hale and R. L. Penn, *CRYSTAL GROWTH & DESIGN*, 2013, **13**, 3396–3403.
27 N. Fomina, C. A. Johnson, A. Maruniak, S. Bahrampour, C. Lang, R. W. Davis, S. Kavusi and H. Ahmad, *LAB ON A CHIP*, 2016, **16**, 2236–2244.
28 R.-Q. Chen, Q.-D. Cheng, J.-J. Chen, D.-S. Sun, L.-B. Ao, D.-W. Li, Q.-Q. Lu and D.-C. Yin, *CRYSTENGCOMM*, 2017, **19**, 860–867.
29 C. Gabriel, M. Perikli, C. P. Raptopoulou, A. Terzis, V. Psycharis, C. Mateescu, T. Jakusch, T. Kiss, M. Bertmer and A. Salifoglou, *INORGANIC CHEMISTRY*, 2012, **51**, 9282–9296.
30 I. Chi-Duran, J. Enriquez, C. Manquian, K. Wrighton-Araneda, W. Canon-Mancisidor, D. Venegas-Yazigi, F. Herrera and D. P. Singh, *ACS OMEGA*, 2018, **3**, 801–807.
31 R. Abazari, A. R. Mahjoub, A. M. Z. Slawin and C. L. Carpenter-Warren, *ULTRASONICS SONOCHEMISTRY*, 2018, **42**, 594–608.
32 Y. Lv, S. Wang, R. Zhang, D. Zhang, H. Yu and G. Lu, *INORGANIC CHEMISTRY COMMUNICATIONS*, 2018, **97**, 30–33.
33 R. Seetharaj, P. V. Vandana, P. Arya and S. Mathew, *ARABIAN JOURNAL OF CHEMISTRY*, 2019, **12**, 295–315.
34 X. Luo, Q. Zhou, S. Du, J. Li, L. Zhang, K. Lin, H. Li, B. Chen, T. Wu, D. Chen, M. Chang and Y. Liu, *ACS APPLIED MATERIALS & INTERFACES*, 2018, **10**, 42335–42347.
35 S. Chui, S. Lo, J. Charmant, A. Orpen and I. Williams, *SCIENCE*, 1999, **283**, 1148–1150.
36 K.-S. Lin, A. K. Adhikari, C.-N. Ku, C.-L. Chiang and H. Kuo, *INTERNATIONAL JOURNAL OF HYDROGEN ENERGY*, 2012, **37**, 13865–13871.
37 A. Raf, J. Ye, S. Zhang, Y. Qi, G. Wang, Y. Che and G. Ning, *DALTON TRANSACTIONS*, 2019, **48**, 17810–17817.
38 A. Kojtari, P. J. Carroll and H.-F. Ji, *CRYSTENGCOMM*, 2014, **16**, 2885–2888.
39 G. W. Peterson, G. W. Wagner, A. Balboa, J. Mahle, T. Sewell and C. J. Karwacki, *JOURNAL OF PHYSICAL CHEMISTRY C*, 2009, **113**, 13906–13917.
40 R. PECH and J. PICKARDT, *ACTA CRYSTALLOGRAPHICA SECTION C-CRYSTAL STRUCTURE COMMUNICATIONS*, 1988, **44**, 992–994.
41 G. Majano, O. Martin, M. Hammes, S. Smeets, C. Baerlocher and J. Perez-Ramirez, *ADVANCED FUNCTIONAL MATERIALS*, 2014, **24**, 3855–3865.
42 C. Prestipino, L. Regli, J. Vitillo, F. Bonino, A. Damin, C. Lamberti, A. Zecchina, P. Solari, K. Kongshaug and S. Bordiga, *CHEMISTRY OF MATERIALS*, 2006, **18**, 1337–1346.
43 N. R. Dhumal, M. P. Singh, J. A. Anderson, J. Kiefer and H. J. Kim, *JOURNAL OF PHYSICAL CHEMISTRY C*, 2016, **120**, 3295–3304.
44 J. Cortes-Suarez, V. Celis-Arias, H. Beltran, I, A. Tejeda-Cruz, I. A. Ibarra, J. E. Romero-Ibarra, E. Sanchez-Gonzalez and S. Loera-Serna, *ACS OMEGA*, 2019, **4**, 5275–5282.
45 N. Marshall, W. James, J. Fulmer, S. Crittenden, A. B. Thompson, P. A. Ward and G. T. Rowe, *INORGANIC CHEMISTRY*, 2019, **58**, 5561–5575.
46 C. Petit, B. Mendoza, D. O'Donnell and T. J. Bandosz, *LANGMUIR*, 2011, **27**, 10234–10242.
47 S. D. Worrall, M. A. Bissett, P. I. Hill, A. P. Rooney, S. J. Haigh, M. P. Attfield and R. A. W. Dryfe, *ELECTROCHIMICA ACTA*, 2016, **222**, 361–369.
48 F. S. Gentile, M. Pannico, M. Causa, G. Mensitieri, G. Di Palma, G. Scherillo and P. Musto, *JOURNAL OF MATERIALS CHEMISTRY A*, 2020, **8**, 10796–10812.