

3-D nanorod arrays of metal–organic KTCNQ semiconductor on textiles for flexible organic electronic†

Cite this: *RSC Advances*, 2013, 3, 17654

Received 27th June 2013,

Accepted 23rd July 2013

DOI: 10.1039/c3ra43291b

www.rsc.org/advances

Rajesh Ramanathan,^a Ahmad Esmailzadeh Kandjani,^a Sumeet Walia,^b Sivacarendran Balendhran,^b Suresh K. Bhargava,^c Kourosh Kalantar-zadeh^b and Vipul Bansal^{*a}

We present a facile and low temperature approach for the fabrication of flexible organic electronic devices by growing high aspect ratio nanorod arrays of potassium 7,7,8,8-tetracyanoquinodimethane (KTCNQ), a crystalline organic semiconductor with charge transfer capabilities, on cotton threads interwoven within the three-dimensional (3-D) matrix of a cotton textile. We demonstrate the capability of this material in developing optoelectronic switches and gas sensors. The ability to grow KTCNQ nanorod arrays in a radial symmetry directly on textiles as a versatile 3-D microtemplate can be extended to the synthesis of a variety of metal–organic charge transfer complexes onto different flexible substrates that can find applications in electronics, catalysis and sensing.

The past decade has seen an increasing research interest towards the development of flexible electronic devices due to their unique properties such as being lightweight, bendable, and portable.¹ It is now widely recognized that the field of flexible electronics holds enormous potential for applications in creating the next generations of photovoltaics,² transistors,³ memristors⁴ and sensors.⁵ Given the increasing importance of this field, the efficient fabrication of the aforementioned flexible devices is of paramount importance.

So far, a wide range of flexible substrates including polymers,⁶ textiles⁷ and foils,⁸ have been employed for the fabrication of electronic devices. Of these, textiles have the potential to gain a special attention due to their use in everyday life, high manoeuvrability, well-established high throughput manufacturing processes and potential economic viability.^{7b} From nanomaterial templating perspective, textiles belong to a class of versatile materials that are

typically porous, flexible, and are woven into a 3-D matrix from individual fibres tens of μm in diameter. These interwoven structures are relatively stable, rich in surface area and exhibit hierarchical ordering.⁹ A novel potential of textiles can be further realised by using them as microtemplates for directly growing nanomaterials and hence incorporating interesting new functionalities.¹⁰

In recent years, an important class of metal–organic semiconducting materials that are based on the charge transfer complexes of metals with 7,7,8,8-tetracyanoquinodimethane (TCNQ) has gained significant attention due to the interesting electronic and optical properties of these materials, which have generated new opportunities for the development of organic devices.¹¹ Amongst these metal–organic complexes, the majority of the recent efforts have been focused on investigating transition metal complexes such as CuTCNQ and AgTCNQ, particularly due to the discoveries made by Dunbar, Bond and Miller *et al.*^{6b,11a,12} Although alkali metal–TCNQ complexes such as LiTCNQ, NaTCNQ and KTCNQ also show interesting electrical charge transportation properties,¹³ these materials have not received their deserved attention for device fabrication, particularly due to the high reactivity of alkali metals and therefore significant challenges associated with their fabrication.¹⁴ Current synthesis strategies for KTCNQ typically employ a rather tedious two-step process, wherein initially through a physical vapour deposition (PVD) process a potassium source (KOH or KI) is evaporated on a substrate in a highly reducing environment at elevated temperatures ($\sim 800^\circ\text{C}$), which is then followed by the reaction of K^+ ions with TCNQ.^{11b,13a,15} Obviously such synthesis strategies, which require harsh conditions, are not compatible with many flexible platforms, in particular textiles.

In the context of textile-based electronic devices, extensive on-going research is focused on employing textiles for supercapacitors and energy storage applications,^{7b,10a} whereas their use as versatile 3-D microtemplates for the synthesis of metal–organic semiconductors has not been attempted. The use of textiles as templates to directly grow metal–TCNQ organic semiconductor complexes with charge transfer capabilities offers unique advantages in terms of low cost, high yield, flexibility, ease of synthesis and robustness.

^aNanoBiotechnology Research Laboratory (NBRL), School of Applied Sciences, RMIT University, GPO Box 2476 V, Melbourne, VIC 3000, Australia.

E-mail: vipul.bansal@rmit.edu.au; Fax: +61 3 9925 3747; Tel: +61 3 9925 2121

^bSchool of Electrical and Computer Engineering, RMIT University, GPO Box 2476 V, Melbourne, VIC 3000, Australia

^cCentre for Advanced Materials and Industrial Chemistry, School of Applied Sciences, RMIT University, GPO Box 2476 V, Melbourne, VIC 3000, Australia

† Electronic supplementary information (ESI) available: Experimental details, additional SEM images, EDX and FTIR spectra. See DOI: 10.1039/c3ra43252a

More importantly, the good absorbent property of cotton-based textiles allows for high binding of ionic reactant species to textile fibres by simple solution immersion. This may facilitate replacement of high temperature PVD fabrication technique in conventional planar substrates with a facile room-temperature solution immersion process in textile-based substrates. In this study, this is demonstrated *via* facile synthesis of KTCNQ nanorod arrays using textile as the underlying template and their application as opto-electronic switches and gas sensing devices.

In our synthesis process (experimental details in supplementary information†), a piece of cotton textile ($1 \times 2 \text{ cm}^2$) was initially immersed in aqueous KOH solution at room temperature followed by a brief period of textile drying. The absorbent properties of cotton textile allowed adherence of high proportions of K^+ and OH^- ions to the textile fibres, without the requirement of high temperature PVD step. This KOH-treated textile was then converted to KTCNQ textile by a single-step chemical vapour deposition (CVD) process using TCNQ powder:



Fig. 1a–b shows the scanning electron microscopy (SEM) images of KTCNQ nanorod arrays grown around the textile fibres in radial symmetry. The surface of all the fibres within the textile 3-D matrix is found to be uniformly decorated with high aspect ratio (~ 100) nanorods of 100–500 nm in diameter and 10–50 μm

in length. The absence of these KTCNQ microrods on the untreated textile surface affirms that the observed structures grow during the CVD process (supplementary information,† Fig. S1). Energy dispersive X-ray (EDX) spectroscopy and mapping of textile surface further affirms the binding of K and TCNQ onto the textile surface after the KOH treatment and CVD process, respectively (Fig. 1c–f). Presence of K energy edges observed in KOH-treated textile that remains consistent after the CVD process affirms strong binding of K^+ ions to the textile. Similarly, an increase in the C energy edge signal in the KTCNQ textile over KOH-treated textile, along with the presence of a new N energy edge in KTCNQ textile, also supports the binding of TCNQ with the textile during CVD process. The EDX spectrum of untreated pristine textile is shown in supplementary information† (Fig. S2), which does not show K or N signatures.

Since EDX spectroscopy cannot differentiate between the chemical nature of TCNQ species (TCNQ^0 in reactant and TCNQ^- in KTCNQ), vibrational spectroscopy (FTIR and Raman) were employed to confirm the presence of a TCNQ^- radical in the textiles (Fig. 2). Comparison of the FTIR spectra of pristine TCNQ powder and KTCNQ textile shows peaks at 2224 and 1545 cm^{-1} characteristic of neutral TCNQ^0 in the first case, while these peaks are shifted to 2180 and 1506 cm^{-1} in the case of textile (Fig. 2a). The shifted peaks in the latter are the characteristic signatures of TCNQ^- species,^{6b,11a} confirming the formation of KTCNQ complexes on the textile surface. The additional FTIR vibrational modes observed in the KTCNQ textile arise from cellulose present in the underlying textile, which are similar to those observed in the untreated and the KOH-treated textiles (supplementary information,† Fig. S3).

Similarly, the comparison of Raman spectra of pristine TCNQ and CVD-processed textile confirmed the formation of KTCNQ on the textile surface (Fig. 2b). The pristine TCNQ shows four principle characteristic Raman vibrational modes at *ca.* 1200 cm^{-1} (C=CH bending), 1450 cm^{-1} (C-CN wing stretching), 1600 cm^{-1} (C=C stretching) and 2225 cm^{-1} (C-N stretching), corresponding to neutral TCNQ^0 .^{6b,11a} Conversely in KTCNQ textile, the original 2225 cm^{-1} stretching band shifts to 2204 cm^{-1} and the band at 1450 cm^{-1} reappears at 1388 cm^{-1} . These shifts in the vibrational modes are typical characteristics of TCNQ^- and they are in alignment with the values reported for KTCNQ crystals.^{6b,11a,16}

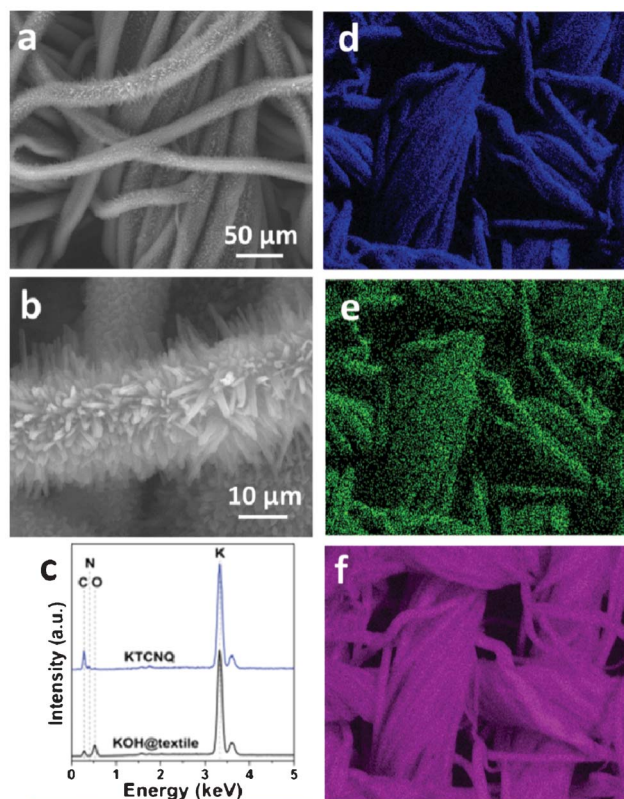


Fig. 1 (a and b) SEM images of KTCNQ nanorod arrays on textile, (c) EDX spectra from KOH-textile and KTCNQ textile, (d–f) EDX spectral maps of KTCNQ textile showing C, N and K (K shells), respectively.

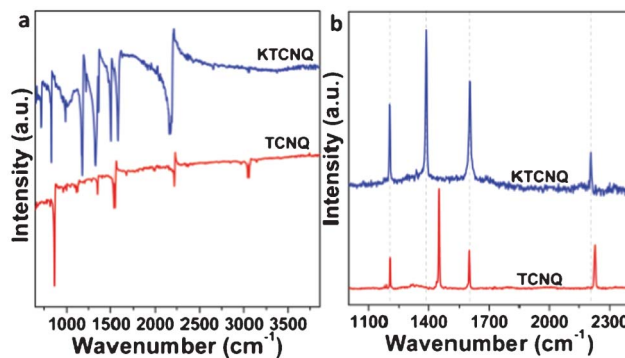


Fig. 2 (a) FTIR and (b) Raman spectra from pristine TCNQ and KTCNQ textiles.

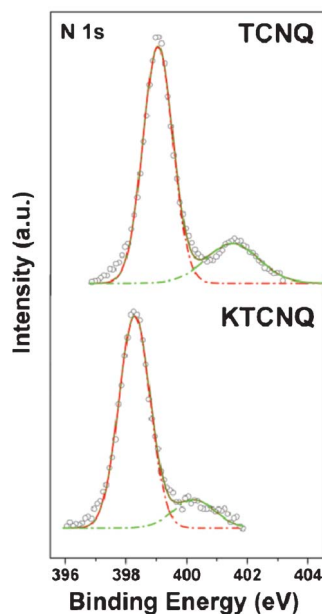


Fig. 3 XPS analysis showing N 1s core levels from pristine TCNQ and KTCNQ textile.

The formation of KTCNQ textile was further validated using X-ray photoelectron spectroscopy (XPS) by comparing the N 2p core levels of pristine TCNQ and KTCNQ textile after background correcting XPS spectra using Shirley algorithm, aligning core level binding energies (BEs) with adventitious C 1s BE of 285 eV, and deconvoluting spectral components using a Gaussian-Lorentzian function (Fig. 3).¹⁷ Neutral TCNQ molecules showed characteristic N 1s core level BE at 399.1 eV along with a shake-up feature at 2.4 eV higher BE.^{6a,18} Conversely, KTCNQ textile showed a significant shift in N 1s core level BE to 398.3 eV along with a concomitant shift in shake-up feature that was at 2.1 eV higher BE in this case. The observed shift of N 1s core level to the lower BE occurs due to the charge transfer from metal to TCNQ molecules, a phenomenon well reported in the case of several TCNQ-based systems.^{6a,18} Additionally, supplementary information,† Fig. S4 shows K 2p core level in KTCNQ textile with a BE maximum at 293.3 eV, confirming the valence state of potassium as ionic K^+ in the KTCNQ fabric.¹⁹

Once the successful fabrication of KTCNQ nanorod arrays on textile surface was validated using the aforementioned tools, the potential applicability of KTCNQ textiles as flexible resistive memory and sensing devices was further assessed. These assessments were preceded by performing temperature and light-dependent conductivity measurements on the fabrics to gain an overall understanding regarding their electronic behaviour. Previously, it has been observed that KTCNQ thin films can switch from a high to a low resistive stage at a particular voltage in response to the electric field.^{13b} When the voltage was applied across KTCNQ textile, a small hysteresis featured due to an electrical switching to a low resistive stage that can be observed at *ca.* 3 V (Fig. 4a). Notably, KTCNQ fabrics showed an interesting temperature-dependent reduction in the current magnitude with an increase in temperature that remained linear between 0–4 V irrespective of temperatures. This inverse dependence of current

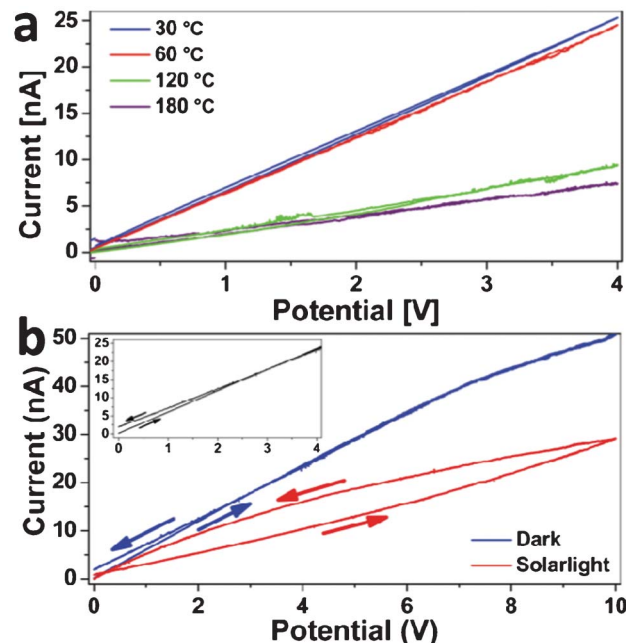


Fig. 4 *I*–*V* curve of the K-TCNQ device (a) at different temperatures (30, 60, 120 and 180 °C), (b) in the absence and presence of solar-light. The inset shows the *I*–*V* curve between 0–4 V in the absence of sunlight.

on temperature is inherent to p-type behaviour, which establishes KTCNQ as a p-type semiconductor. To the best of the authors' knowledge, the p-type nature of KTCNQ organic semiconductors has not been demonstrated previously, which should now open avenues for exploring these materials for new applications.

Since metal-TCNQ organic charge transfer complexes typically show an electrical response to light,²⁰ current-voltage (*I*–*V*) measurements were also performed while exciting KTCNQ textile with a standard simulated sun light source at 1.5 sun (Fig. 4b). Upon exposure to the sun simulator at room temperature, a pronounced hysteresis *I*–*V* feature, due to the switching of KTCNQ from a high to a low resistive stage is observed. This establishes the photoelectric switching behaviour in KTCNQ-based materials, and allows KTCNQ textiles to be used as organic opto-electric memory devices.¹⁶ The reduction of the resistance after its exposure to the sun simulator light is also evidence that KTCNQ is a p-type semiconductor.

Given the semiconducting property of the developed material, we further employed these highly porous and flexible KTCNQ textiles as toxic gas sensing devices for room-temperature nitrogen dioxide (NO_2) sensing (Fig. 5). NO_2 was chosen, as according to Jouve *et al.*, it produces the largest response amongst the oxidizing gases when exposed to the sensitive film of materials from TCNQ family.²¹ Before the NO_2 exposure, the fabricated KTCNQ device showed ~ 7 M Ω resistance, which on exposure to 10 ppm of NO_2 gas (in ambient air background), decreased significantly ($>10\%$ change). Each exposure to NO_2 gas was followed by an exposure to air to understand the reversibility of these materials. It has been reported that the presence of NO_2 gas molecules strongly alters the conduction between dendritic paths in TCNQ compounds.^{21,22}

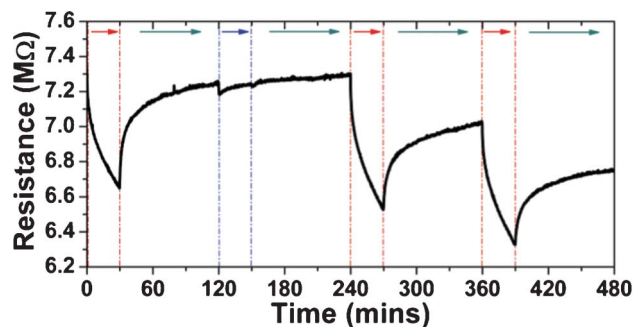


Fig. 5 Sensing curve for NO_2 and H_2 gas species at 10 ppm and 10 000 ppm in ambient air (zero air with no humidity) using KTCNQ fabric. Each cycle represents either exposure to sensor gas (red arrow – NO_2 and blue arrow – H_2) or flushing with compressed air (green arrow).

Inclusion of K atoms into the compound modifies the nature of the interaction and probably allows weaker bonds between the NO_2 gas molecules and KTCNQ compound to occur due to the strong polarisability that is granted to the system by the large K atoms. As a result, a partial reversibility towards NO_2 is gained when KTCNQ is used as the sensitive material for NO_2 gas sensing. Obviously, the high surface to volume ratio of the KTCNQ flexible template, made of nanorods, significantly increased the response magnitude and consequently the sensitivity of the device. Additionally, the sensing property of the KTCNQ compound was tested against H_2 gas (1% in ambient air, *i.e.* 10 000 ppm) which is a typical reducing gas. Fig. 5 shows that the exposure to H_2 at 120 min time point, wherein only a 0.5% drop in resistance is observed in the first minute that is followed by desorption of the gas from the sensing device. As a result, KTCNQ, similar to other TCNQ compounds, appear to show specificity only to oxidising gas species.^{21,22}

In summary, we demonstrate a facile approach for fabricating high aspect ratio KTCNQ nanorod arrays on flexible textile substrates. Additionally, we report a method that allows K^+ ions to be directly converted to KTCNQ without involving a high temperature potassium deposition step. This was particularly necessary for the synthesis of nanorod arrays onto textiles that can only survive low temperature processes. Altogether, this study proves the possibility of growing metal-TCNQ charge transfer complexes on flexible textile substrates, which shows applicability for flexible electronics and sensing. As proof-of-concept of our approach, the applicability of KTCNQ textile devices for photo-electric switching and NO_2 gas sensing is shown. The materials show a p-type semiconducting nature, showing a partial reversibility in response to an oxidising gas such as NO_2 , owing to the incorporation of the K atoms, and no response to a reducing gas such as H_2 . The developed complex has a great potential to be used in future flexible optical, electrical, sensing and catalytic systems.

Acknowledgements

V. Bansal thanks the Australian Research Council for research funding through the Discovery and Linkage grant schemes. V.

Bansal also acknowledges the support of the Ian Potter Foundation to establish a multimode spectroscopy facility at RMIT University, which were used in this study. The instrument and technical support from the RMIT Microscopy and Microanalysis Facility is duly acknowledged.

Notes and references

- 1 I. Park, S. H. Ko, H. Pan, C. P. Grigoropoulos, A. P. Pisano, J. M. J. Fréchet, E. S. Lee and J. H. Jeong, *Adv. Mater.*, 2008, **20**, 489–496.
- 2 (a) Z. Fan, H. Razavi, J. Do, A. Moriwaki, O. Ergen, Y. L. Chueh, P. W. Leu, J. C. Ho, T. Takahashi and L. A. Reichertz, *Nat. Mater.*, 2009, **8**, 648–653; (b) L. Gomez De Arco, Y. Zhang, C. W. Schlenker, K. Ryu, M. E. Thompson and C. Zhou, *ACS Nano*, 2010, **4**, 2865–2873.
- 3 (a) K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano and H. Hosono, *Nature*, 2004, **432**, 488–492; (b) Q. Cao, S. H. Hur, Z. T. Zhu, Y. G. Sun, C. J. Wang, M. A. Meitl, M. Shim and J. A. Rogers, *Adv. Mater.*, 2006, **18**, 304–309.
- 4 D. I. Son, T. W. Kim, J. H. Shim, J. H. Jung, D. U. Lee, J. M. Lee, W. I. Park and W. K. Choi, *Nano Lett.*, 2010, **10**, 2441–2447.
- 5 (a) M. C. McAlpine, H. Ahmad, D. Wang and J. R. Heath, *Nat. Mater.*, 2007, **6**, 379–384; (b) S. Park, G. Wang, B. Cho, Y. Kim, S. Song, Y. Ji, M. H. Yoon and T. Lee, *Nat. Nanotechnol.*, 2012, **7**, 438–442.
- 6 (a) J. M. Lindquist and J. C. Hemminger, *Chem. Mater.*, 1989, **1**, 72–78; (b) A. Pearson, A. P. O'Mullane, S. K. Bhargava and V. Bansal, *Inorg. Chem.*, 2012, **51**, 8791–8801.
- 7 (a) M. Panhuis, J. Wu, S. A. Ashraf and G. G. Wallace, *Synth. Met.*, 2007, **157**, 358–362; (b) L. Hu and Y. Cui, *Energy Environ. Sci.*, 2012, **5**, 6423–6435.
- 8 V. Zardetto, T. M. Brown, A. Reale and A. Di Carlo, *J. Polym. Sci., Part B: Polym. Phys.*, 2011, **49**, 638–648.
- 9 A. N. Nakagaito, M. Nogi and H. Yano, *MRS Bull.*, 2010, **35**, 214–218.
- 10 (a) L. Hu, M. Pasta, F. L. Mantia, L. Cui, S. Jeong, H. D. Deshazer, J. W. Choi, S. M. Han and Y. Cui, *Nano Lett.*, 2010, **10**, 708–714; (b) M. Catrysse, R. Puer, C. Hertleer, L. Van Langenhove, H. van Egmond and D. Matthys, *Sens. Actuators, A*, 2004, **114**, 302–311.
- 11 (a) A. Pearson, A. P. O'Mullane, V. Bansal and S. K. Bhargava, *Inorg. Chem.*, 2011, **50**, 1705–1712; (b) C. Wackerlin, C. Iacovita, D. Chylarecka, P. Fesser, T. A. Jung and N. Ballav, *Chem. Commun.*, 2011, **47**, 9146–9148.
- 12 (a) H. Miyasaka, N. Motokawa, S. Matsunaga, M. Yamashita, K. Sugimoto, T. Mori, N. Toyota and K. R. Dunbar, *J. Am. Chem. Soc.*, 2010, **132**, 1532–1544; (b) E. B. Vickers, T. D. Selby, M. S. Thorum, M. L. Taliaferro and J. S. Miller, *Inorg. Chem.*, 2004, **43**, 6414–6420; (c) A. K. Neufeld, A. P. O'Mullane and A. M. Bond, *J. Am. Chem. Soc.*, 2005, **127**, 13846–13853.
- 13 (a) L. Melby, R. Harder, W. Hertler, W. Mahler, R. Benson and W. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374–3387; (b) X.-L. Mo, G.-R. Chen, Q.-J. Cai, Z.-Y. Fan, H.-H. Xu, Y. Yao, J. Yang, H.-H. Gu and Z.-Y. Hua, *Thin Solid Films*, 2003, **436**, 259–263.
- 14 M. Caragiu and S. Finberg, *J. Phys.: Condens. Matter*, 2005, **17**, R995.
- 15 (a) A. Funabiki, T. Mochida, K. Takahashi, H. Mori, T. Sakurai, H. Ohta and M. Uruichi, *J. Mater. Chem.*, 2012, **22**, 8361–8366; (b) J. L. Goudard, A. A. Lakhani and N. K. Hota, *Solid State Commun.*, 1982, **41**, 423–426.

- 16 K. Xiao, J. Tao, Z. Pan, A. A. Puretzky, I. N. Ivanov, S. J. Pennycook and D. B. Geohegan, *Angew. Chem., Int. Ed.*, 2007, **46**, 2650–2654.
- 17 (a) V. Bansal, A. Ahmad and M. Sastry, *J. Am. Chem. Soc.*, 2006, **128**, 14059–14066; (b) R. Ramanathan, J. L. Campbell, S. K. Soni, S. K. Bhargava and V. Bansal, *PLoS One*, 2011, **6**(3), e17707.
- 18 J. M. Lindquist and J. C. Hemminger, *J. Phys. Chem.*, 1988, **92**, 1394–1396.
- 19 J. Hasselström, A. Föhlisch, R. Denecke, A. Nilsson and F. De Groot, *Phys. Rev. B: Condens. Matter*, 2000, **62**, 11192.
- 20 J. B. Torrance, B. A. Scott and F. B. Kaufman, *Solid State Commun.*, 1975, **17**, 1369–1373.
- 21 C. Jouve, D. Jullien and B. Remaki, *Sens. Actuators, B*, 1995, **28**, 75–80.
- 22 K.-C. Ho and J.-Y. Liao, *Sens. Actuators, B*, 2003, **93**, 370–378.