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High-pressure hydrogenation of graphene: towards graphane†

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The conversion of graphene to graphane is of high importance from a technological and scientific point of view. We present here a scalable method for the hydrogenation of graphene based on thermal exfoliation of graphite oxide in a hydrogen atmosphere under high pressure (60–150 bar) and temperature (200–500 °C). This method does not require a plasma source and is able to produce gram quantities of the material. The properties of the resultant hydrogenated graphene were studied by scanning and transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, infrared spectroscopy and combustible elemental analysis techniques. Sheet and specific resistance of the graphene and hydrogenated graphene were measured. This scalable synthesis method has great potential to serve as a pathway towards the mass production of graphane.

Introduction

Graphene is currently one of the highly researched materials. The idea of incorporating a single-atom thick¹ conductive sheet with excellent thermal conductivity, fast heterogeneous electron transfer, and a huge surface area into functional devices has quickly found its way to physicists, chemists and materials scientists.^{2–5} Graphane is a hydrogenated analogue of graphene consisting of sheets of sp³ bonded carbon atoms which could be an interesting alternative material to graphene. The theoretical explanation for the existence of graphane has surfaced several years ago⁶ and experimental attempts for preparation of the material have begun in 2009.⁷ It is expected that graphane will behave similar to an electrical insulator that possesses a huge surface area and high C : H ratio with potential use for hydrogen storage.⁸ Partial hydrogenation of graphene is anticipated to result in the opening of the graphene bandgap which allows the material to have huge implications towards the fabrication of atomically thin transistors⁹ or electrochemical devices.¹⁰ In addition, graphane can be used as an anticorrosion protective layer for metallic structures.

Currently, few publications reporting on the preparation of graphanes and their resulting properties are available. One of the earliest reports showed that such graphanes were achieved through the hydrogenation of CVD graphene in low-pressure (0.1 mbar) hydrogen–argon mixture with DC-plasma.⁷ Plasma hydrogenation at pressures of ~2 mbar to produce graphanes was also carried out on CVD graphene with a reported

hydrogenation efficiency of <10%.¹¹ Similar results were obtained with multilayer graphene prepared from mechanically cleaved highly oriented pyrolytic graphite using radio frequency plasma hydrogenation, which was executed to produce graphanes with a reported efficiency of ~17%.¹² It is of interest to mention that through the execution of theoretical calculations, it was discovered that single-sided hydrogenated graphene is thermodynamically stable to have a coverage of maximum of ~12%.¹³ The above-mentioned methods were carried out with minute amounts of graphene, prepared either by CVD growth or mechanical cleavage. Although these methods are certainly important towards the study on the fundamental chemistry of graphene/graphane, the need for scalable methods to produce bulk quantities of graphane is still greatly in demand. Herein we propose one such straightforward method where the use of high-pressure (up to 150 bar) and temperature (up to 500 °C) in the hydrogenation of graphite oxide is capable of yielding large quantities of partially hydrogenated graphane sheets.

Experimental section

SEM imaging was performed with a JEOL 7600F field-emission scanning electron microscope (JEOL, Japan) in gentle-beam mode at 2 kV. The samples were prepared by attaching the materials onto a sticky conductive carbon tape and mounting it on an aluminium sample stub. TEM images were acquired with a JEM 1400 field-emission transmission electron microscope (JEOL, Japan) operating at 100 kV. TEM samples were prepared using 1 µL of a 0.5 mg mL^{−1} suspension of the thermally reduced graphenes dripped onto a carbon coated copper grid which was then allowed to dry at room temperature. XPS was executed with a Phoibos 100 spectrometer using a monochromatic Mg X-ray radiation source (SPECS, Germany) for the measurement of wide-scan and high resolution C 1s spectra. The samples were attached onto a sticky conductive carbon tape that was attached

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to an aluminium XPS holder. Further processing of the data was performed by calculating the C/O ratios from the wide-scan XPS measurements with the use of relative sensitivity factors. The XPS samples were prepared by attaching a uniform layer of the materials onto a conductive carbon tape which was then affixed onto an aluminium XPS sample holder. A confocal micro-Raman LabRam HR instrument (Horiba Scientific) in back-scattering geometry with a CCD detector was used for acquiring Raman spectra. Measurements were performed using a 514.5 nm Ar laser and an Olympus optical microscope with a 100 $\times$ objective lens. Pre-measurement calibration was achieved with a silicon reference at 520 cm⁻¹ which gives a peak position resolution of less than 1 cm⁻¹. Actual measurements were performed using well-compressed and compacted samples that were placed on top of a glass slip which was positioned on a piece of glass slide. The Fourier transform infrared spectroscopic measurements were performed using an attenuated total reflectance method on a PerkinElmer Spectrum 100 system. Diamond/ZnSe was used as the ATR crystal in conjunction with a universal ATR accessory. For conductivity measurements of graphene related materials, 40 mg of the material were first compressed into a capsule (1/4" diameter) under a pressure of 400 MPa for 30 s. The resistivity of the resulting capsule was measured with a 4-probe technique using the method of van der Pauw.¹⁴ The resistivity measurements were then performed with a Keithley 6220 current source and an Agilent 34970A data acquisition/switch unit.

The graphene oxide that was used for the synthesis of partially hydrogenated graphane was prepared according to the Hofmann method that had previously been reported.¹⁵ 87.5 mL of sulphuric acid (98%) and 27 mL of nitric acid (65%) were added to a reaction flask (Pyrex baker with thermometer) which contains a magnetic stir bar. The mixture was then cooled by immersing it into an ice bath for 30 min. 5 g of graphite was then added to the mixture under vigorous stirring to avoid agglomeration and to obtain a homogeneous dispersion. While maintaining the reaction flask in the ice bath, 55 g of potassium chlorate was then slowly added to the mixture (over 30 min) in order to avoid a sudden increment in temperature and the formation of the explosive chlorine dioxide gas. Upon complete dissolution of potassium chlorate, the reaction flask was left loosely capped to allow the evolution of gas and the mixture was then stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5%) solution to remove sulphate ions and repeatedly centrifuged and redispersed in deionized water until a negative response towards chloride and sulphate ions (with AgNO₃ and Ba(NO₃)₂, respectively) was achieved. The graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

The high pressure synthesis of the materials was performed in a stainless steel autoclave placed in a resistive heating furnace. Approximately 0.3 g of graphite oxide was placed in a quartz glass liner inside the autoclave machine. Hydrogen gas of 99.9% purity and argon gas of 99.996% purity were used in the synthesis process. The autoclave was then repeatedly flushed with hydrogen or argon gas and subsequently filled with the respective gases of the desired pressure using a pressure control valve. The autoclave was heated at a rate of 5 °C min⁻¹ and the dwell time on the temperature of synthesis was 2 hours. The reaction vessel

was then left to cool freely inside the furnace under room temperature.

Results and discussion

The presented method uses a high pressure/high temperature exfoliation procedure on graphite oxide carried out in a hydrogen gas atmosphere, which results in the material being partially hydrogenated. We have also studied the influence of temperature and pressure on the properties of the resulting hydrogenated graphene sheets by systematically varying the exfoliation conditions of graphite oxides. Before further discussions on the characterization results are elaborated, one should ask himself the fundamental question: which method is the most appropriate in determining the hydrogenation efficiency of the materials? Previously, it was correctly stated that "it is quite difficult to measure the percentage of hydrogen content in graphene films by most surface analytical techniques".¹¹ Indeed, these methods can only provide indirect and/or approximate information on the hydrogen coverage of the materials. An example of such a method that provides indirect information is Raman spectroscopy or conductivity measurements. There is no accurate method including X-ray photoelectron spectroscopy (XPS) which is based on the analysis of the C 1s peak to provide some information on the presence of the C–H bond. However, the narrow difference between bond energies of C–H and C=C bonds (difference of only 0.6 eV) makes any accurate conclusion on hydrogen coverage impossible. In contrast, chemical analysis based on the rotation/vibration modes of the bonds (infrared spectroscopy) allows C–H and C=C bonds to be distinguished with greater certainty. To date, the most precise and accurate measurements on the hydrogenation efficiency can only be derived by the classical combustible elemental analysis technique. It is also of interest to note that none of the earlier reports have utilised infrared spectroscopy or combustible elemental analysis to analyse the extent of hydrogenation in the materials.^{7,11,12} This is likely due to the fact that the graphanes were synthesized from minute amounts of graphene grown by the CVD method and hence, the small amount of material available is unsuitable for the implementation of the mentioned techniques. The lack of evidence derived from the FT-IR spectroscopy and elemental analysis implies that any earlier claims on the hydrogenation of graphene are least reliable and ambiguous. Herein, all available materials and chemical analysis methods were employed to investigate the effect on hydrogenation efficiency under varied exfoliation conditions. These methods include scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR) and combustible elemental analysis (EA).

Two different sets of reaction conditions were employed to study the influence of hydrogen pressure and exfoliation temperature on the properties of the materials. In the first experiment, the temperature was held constant at approximately 220 °C while the hydrogen gas pressure was varied between 60 and 150 bar during the exfoliation process. In the second experiment, the hydrogen gas pressure was held constant at 100 bar while the exfoliation temperature was varied from 200 to 500 °C instead. For the control experiment, graphene exfoliated

in an inert gas (argon) atmosphere will be used for comparison with the hydrogenated graphenes. In this paper, the materials will be denoted by their exfoliation conditions in terms of temperature and gas pressure, *e.g.* graphene exfoliated under 100 bar hydrogen gas pressure at 500 °C will be labelled as G-H: [100 bar/500 °C].

As unexfoliated graphite oxide was used as the starting material in this project, we will first examine the exfoliated/hydrogenated graphenes (final product) with electron microscopy to confirm the successful exfoliation of the graphite oxides. Fig. S1 (see ESI†) shows the SEM images of the control sample and graphenes hydrogenated under different pressures and temperatures taken at different magnifications. It can be clearly observed from the SEM images that exfoliation of the graphite oxides has successfully taken place and that no observable differences between the various hydrogenated graphenes and the control sample can be noted. TEM imaging of the hydrogenated graphene sheets (as well as control graphene exfoliated in Ar) was also performed as shown in Fig. S2 (see ESI†) to observe single to few layer sheets of graphene/graphane. It was observed that graphenes exfoliated under high temperatures of 350 °C and 500 °C (at 100 bar pressure) exhibit a wrinkled appearance when compared to other graphenes which showed a much smoother texture and a straight or flat appearance. Wrinkling of graphene can be both due to the high concentration of heptagon/pentagon rings in the wrinkle or the hydrogenation of graphene (note that the hydrogenated 6 member ring does not exhibit a 2D structure). However, no other major difference between the different hydrogenated graphenes and the control sample is observable through TEM. In summary, SEM and TEM results have confirmed that effective exfoliation of graphite oxide under hydrogen atmosphere at high gas pressures occurs in a similar manner as that in an inert gas atmosphere.

Consequently, we have investigated the density of defects in the hydrogenated graphenes and the influence of the hydrogenation conditions on such density of defects using Raman spectroscopy analysis. The Raman spectroscopic technique generates two distinct peaks at $\sim 1300\text{ cm}^{-1}$ and $\sim 1590\text{ cm}^{-1}$ which correspond to defects in the sp^2 lattice network (D peak) and the sp^2 hybridized carbon (G peak), respectively. Using the ratio of the intensities of the D and G peaks, it is also possible to calculate the crystallite size of sp^2 graphene according to the equation:¹⁶

$$L_a = 2.4 \times 10^{-10} \times \lambda_{\text{laser}}^4 \times I_G/I_D$$

where I_G and I_D are the intensities of the D and G bands and λ_{laser} is the wavelength of the laser in nm.

As shown in Fig. 1, the Raman spectra are presented for the range of wavenumbers from 1000 cm^{-1} to 3000 cm^{-1} for comparison between the different graphite oxides. It can be clearly observed from Fig. 1A (top part) that the D/G ratio increases from 0.85 to 1.10 (crystallite size decreases from 19.71 to 15.23 nm) with increasing exfoliation gas pressure from 60 bar to 150 bar (under a constant temperature of $\sim 220\text{ °C}$). This may be due to the increasing amount of defects being introduced when higher hydrogen gas pressure is used during exfoliation/hydrogenation of the graphite oxides. This relationship is demonstrated in a graphical plot shown in Fig. 1A (bottom part). Moreover, it is important to note that special care was taken to

ensure that a reproducible and consistent result was obtained for the Raman spectroscopic characterization by calculating an average ratio from a total of nine measurements which were taken at different positions on the specimen. In Fig. 1B, the Raman spectra of graphenes hydrogenated under increasing temperatures from 200 to 500 °C but at a constant gas pressure of 100 bar are presented. It was found that the D/G ratio decreases with increasing exfoliation temperature from 0.87 for graphene exfoliated at 200 °C (crystallite size: 19.26 nm) to 0.77 for an exfoliation temperature of 350 °C (crystallite size: 21.76 nm) before levelling off to 0.81 for the exfoliation temperature of 500 °C ($L_a = 20.68\text{ nm}$). Graphene exfoliated in an argon atmosphere was measured to give a D/G ratio of 0.78 ($L_a = 21.37\text{ nm}$). Therefore, it was discovered that all hydrogenated graphenes have a higher density of defects than graphenes exfoliated in argon. This is likely due to the fact that in addition to the introduction of defects into the materials during the exfoliation process (demonstrated by the control sample exfoliated in an Ar atmosphere), a partial hydrogenation of the graphene may have occurred. Since Raman spectroscopy is an indirect method for the investigation of the density of hydrogenated sites, the hydrogenation efficiency of the materials will be further explored with an alternative technique, XPS.

X-ray photoelectron spectroscopy (XPS) is a useful method for the determination of the chemical composition at the surface of the materials. Herein, a wide-scan XPS measurement is performed to determine if any possible removal of the oxygen containing groups from the graphite oxide surfaces during exfoliation/hydrogenation may have occurred. The wide-scan XPS spectra of graphenes exfoliated under increasing gas pressures (constant temperature) and graphenes exfoliated under increasing temperatures (constant gas pressure) are shown in Fig. S3A and B,† respectively. It is evident that an increasing gas pressure applied during exfoliation has a negative influence on the removal of oxygen containing groups, where G-H: [150 bar/220 °C] contains significantly more oxygen containing groups than G-H: [60 bar/220 °C]. The oxygen content in the material is reflected in the C/O ratio calculated, where a sharp decrease in the ratio from 7.2 to 5.0 was observed with increasing hydrogenation gas pressures from 60 to 150 bar (Fig. S3A†). The increasing temperature of exfoliation (constant pressure of 100 bar) resulted in a greater ease in the removal of oxygen containing groups where the C/O ratio was found to increase significantly from 7.1 to 13.0 when the temperature increases from 200 to 500 °C.

High-resolution XPS spectra provide detailed information on the type of chemical bonds present between the atoms that are useful for the chemical analysis at the surface of the materials. However, its application in the determination of the degree of hydrogenation (and for the study of the sp^3/sp^2 ratio on graphene surfaces) is still questionable due to the narrow difference in the bond energies of C=C and C–C bonds as mentioned earlier. Therefore, a strong overlap of the C=C and C–C bands is expected where fitting of the spectra must be performed to clearly separate the bands. Such a fitting has previously been reported to provide information on the quantification of the degree of hydrogenation efficiency on the graphene surfaces¹² as well as on carbon nanotubes.¹⁷ The high-resolution C 1s XPS spectra for all the exfoliated graphenes are shown in Fig. S4.† Relative

Fig. 1 Raman spectra of hydrogenated graphenes under (A) a constant temperature of ~ 220 °C and pressures of (a) 60, (b) 100 and (c) 150 bar and under (B) a constant pressure of 100 bar and varying temperatures of (a) 200, (b) 350 and (c) 500 °C. Also shown are Raman spectra of graphite oxide exfoliated in an Ar atmosphere (d).

sensitivity factors were considered in the fitting of the spectra which was executed in accordance with the bond energies of the various possible carbon–carbon and carbon–oxygen bonds that could be present in the materials. Fitting of the results was performed with the bond energy of C=C at 284.4 eV (red), C–C/C–H bonds at 285.1 eV (blue), C–O bonds at 286.2 eV (cyan), C=O bands at 287.4 eV (purple), O–C=O bonds at 288.7 eV (dark navy) and π – π^* interactions at 290.3 eV (green). The intensity of the C–C/C–H bond was between 12 and 17% of the total sum of the C 1s signals fitted for the hydrogenated graphenes. Percentage of the C–C bonds obtained from the fitting for the control sample's (exfoliated in argon) spectrum was found to account for approximately 16% of the total C 1s signal. Further confirmation of the C–H bonds can be accomplished by the use of IR spectroscopy.

Infrared spectroscopy utilizes a near infra-red beam to induce the various stretching and bending motions of the bonds that occur at frequencies unique to the particular bond and thus, is able to act as a form of identification. The C–H stretching of alkyl carbons occurs at frequencies from 2950 to 2850 cm⁻¹ and was found to be present in the spectra for all the hydrogenated graphenes as shown in Fig. 2. The presence of this stretching

band is identical to that in the recorded spectra for hydrogenated carbon nanotubes and fullerenes that were previously reported.^{17,18} However, this was not observed in the same region of the FT-IR spectra for the control sample where the graphenes are exfoliated in an argon environment and also for the graphite oxides that were used as the starting materials.

The best approach in proving the presence and to measure the degree of hydrogenation efficiency of the materials will be to conduct a combustion elemental analysis. It was revealed that the starting material for this project, graphite oxides, contained 50.64% of C, 20.82% of H and 28.54% of O. With the combination of the data from the combustion elemental analysis and the results obtained from infrared spectroscopy, it can be ascertained that all the H atoms in graphene oxides are bonded to the oxygen atoms present in the starting material, graphene oxides. Graphene exfoliated in argon was found to have a composition of 77.67% of C, 10.35% of H and 11.98% of O. Similarly, earlier FT-IR results coupled with the elemental analysis data have proved the direct attachment of H atoms to the oxygen atoms in G-Ar: [100 bar/350 °C] to form hydroxyl groups, according to the stoichiometry of O and H atoms. Graphene exfoliated under high pressure/temperature in a

Fig. 2 FT-IR spectra of hydrogenated graphenes under (A) a constant temperature of ~ 220 °C and pressures of (a) 60, (b) 100 and (c) 150 bar and under (B) a constant pressure of 100 bar and varying temperatures of (a) 200, (b) 350 and (c) 500 °C. Also shown are Raman spectra of graphite oxide exfoliated in (d) an Ar atmosphere, (e) hydrogen and (f) a hydrogen atmosphere at a pressure of 1 bar.

hydrogen gas atmosphere (G-H: [100 bar/500 °C]) displays a composition of 80.55% of C, 11.6% of H and 7.84% of O. If it was assumed that all the oxygen atoms present in this graphene were bonded to hydrogen atoms to form the -OH stoichiometry, it can be further deduced that the remaining 3.76% of hydrogen is bonded directly to the carbon backbone to give graphanes. In fact, the O_1H_1 stoichiometry is extreme and it is likely that there are carboxyl and carbonyl groups present with O_2H_1 or O_1H_0 stoichiometry; therefore the deduced 3.76% of H in the form of C–H bond is the lowest assumption and the real amount is likely to be higher. This deduction on the existence of the C–H bond in G-H: [100 bar/500 °C] was supported by both the elemental analysis results and the infrared spectroscopic data which were also in good quantitative agreement with the HR-XPS data. It is also of importance to note that a high gas pressure is required for the successful hydrogenation reaction of graphene. Graphite oxides exfoliated in a hydrogen gas atmosphere at a pressure of 1 bar and temperature of 1000 °C possessed an elemental composition of 94.25% of C, 0% of H and 5.75% of O. Similarly, graphenes prepared in a N_2 atmosphere of 1 bar pressure at 1000 °C exhibited an elemental composition of 93.50% of C, 0% of H and 6.50% of O.

We investigated the conductivity of GO, hydrogenated graphene and graphene. GO exhibited a sheet resistivity of $2.176 \times 10^3 \Omega \square^{-1}$ and specific resistivity of $3.67 \times 10^2 \Omega \text{ cm}$; G-H: [100 bar/500 °C] has a sheet resistivity of $1.26 \Omega \square^{-1}$ and specific resistivity of $3.6 \times 10^{-2} \Omega \text{ cm}$; G-Ar: [100 bar/500 °C] possesses a sheet resistivity of $1.14 \Omega \square^{-1}$ and specific resistivity of $2.24 \times 10^{-2} \Omega \text{ cm}$. These values showed that hydrogenated graphene exhibits a larger resistivity than non-hydrogenated graphene which is consistent with the theoretical prediction.

Conclusions

In summary, we have successfully proved that exfoliation of graphite oxides in a hydrogen gas atmosphere under high pressure/temperature conditions can result in a hydrogenation of the graphenes. This was fully supported by an observation of a lack of hydrogenation in graphenes exfoliated under similar conditions but in a non-hydrogen gas environment. Further understanding of the materials was realised through an investigation of the impact of the reaction conditions on the hydrogenation efficiency of the materials. The method using a H_2 pressure of 100 bar at 500 °C was found to be the most efficient reaction condition towards the synthesis of hydrogenated graphene. The synthesis method presented in this paper is of utmost importance due to its scalable capability (in contrast to previously published work where the yield is in limited minute amounts) and thus, effectively producing large amounts of the hydrogenated graphene end product which can be useful towards the fabrication of graphane.

Notes and references

- 1 E. Fitzer, K.-H. Kochling, H. P. Boehm and H. Marsh, *Pure Appl. Chem.*, 1995, **67**, 491.
- 2 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666.
- 3 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183.
- 4 Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts and R. S. Ruoff, *Adv. Mater.*, 2010, **22**, 3906.
- 5 M. Pumera, *Chem. Rec.*, 2012, **12**, 201.
- 6 J. O. Sofo, A. S. Chaudhari and G. D. Barber, *J. Phys. Chem. B*, 2007, **75**, 153401.
- 7 D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov,

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- M. I. Katsnelson, A. K. Geim and K. S. Novoselov, *Science*, 2009, **323**, 610.
- 8 J. Agbenyega, *Mater. Today*, 2009, **12**, 6.
- 9 B. Gharekhanlou and S. Khorasani, *IEEE Trans. Electron Devices*, 2010, **57**, 209.
- 10 M. Pumera, *Chem. Soc. Rev.*, 2010, **39**, 4146.
- 11 J. S. Burgess, B. R. Matis, J. T. Robinson, F. A. Bulat, F. K. Perkins, B. H. Houston and J. W. Baldwin, *Carbon*, 2011, **49**, 4420.
- 12 Z. Luo, T. Yu, K.-J. Kim, Z. Ni, Y. You, S. Lim, Z. Shen, S. Wang and J. Lin, *ACS Nano*, 2009, **3**, 1781.
- 13 H. J. Xiang, E. J. Kan, S.-H. Wei, X. G. Gong and M.-H. Whangbo, *J. Phys. Chem. B*, 2010, **82**, 165425.
- 14 L. J. Van der Pauw, *Philips Res. Rep.*, 1958, **13**, 1.
- 15 H. L. Poh, F. Šaněk, A. Ambrosi, G. Zhao, Z. Sofer and M. Pumera, *Nanoscale*, 2012, **4**, 3515.
- 16 L. G. Cancado, K. Takai, T. Enoki, M. Endo, Y. A. Kim, H. Mizusaki, A. Jorio, L. N. Coelho, R. Magalhaes-Paniago and M. A. Pimenta, *Appl. Phys. Lett.*, 2006, **88**, 163106.
- 17 A. V. Talyzin, S. Luzan, I. V. Anoshkin, A. G. Nasibulin, H. Jiang, E. I. Kauppinen, V. M. Mikoushkin, V. V. Shnitov, D. E. Marchenko and D. Noreus, *ACS Nano*, 2011, **5**, 5132.
- 18 A. V. Talyzin, Y. O. Tsybin, J. M. Purcell, T. M. Schaub, Y. M. Shulga, D. Noreus, T. Sato, A. Dzwilewski, B. Sundqvist and A. G. Marshall, *J. Phys. Chem. A*, 2006, **110**, 8528.