Bull. Mater. Sci., Vol. 37, No. 6, October 2014, pp. 1383–1387. © Indian Academy of Sciences.

# Laser-induced transformation of GaS and GaSe nanosheets to onion structures with closed cages

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MS received 22 April 2014

**Abstract. Experimental evidence for the transformation of nanosheets of GaS and GaSe into onion structures on UV excimer pulsed laser irradiation is presented. Few-layer GaS and GaSe on Si substrates were exposed to KrF pulsed laser with wavelength of 248 nm and the effect was studied as a function of number of laser pulses. Laser-induced dewetting of the layers results in the formation of spherical nanoparticles after 50 laser pulses. HREM images of these particles reveal the formation of onions with several concentric layers. The initial thickness of the layers controls the size of the onion cages. A mechanism of transformation of few layers to closed cage onions on UV pulsed laser irradiation is presented.**

**Keywords.** 2D layered materials; few-layer GaS and GaSe; laser induced dewetting; giant onions and Raman scattering.

## 1. Introduction

Carbon nanotubes and fullerenes formed by rolling and wrapping of graphene layers have captivated the scientific community for some time. Recent investigations have shown that graphene has a tendency to roll-up or wrap-up to transform to a 1D nanotube or a 0D buckyball (Rao *et al* 2004; Chuvilin *et al* 2010; Kit *et al* 2012; Quintana *et al* 2012; Lim *et al* 2013). Apart from carbon, there has been intensive research on tubular and closed cage structures of sulphide, nitride and oxide materials. Layered inorganic transition metal dichalcogenides, $MoS_2$ and $WS_2$, are well explored materials forming nanotubes and fullerene-like structures (Nath and Rao 2001; Nath *et al* 2001; Rao and Nath 2003; Tenne and Rao 2004; Tenne 2006). Unlike graphene, these 2D layered materials do not have dangling bonds on the basal (0 0 0 1) plane perpendicular to the *c*-axis ($\perp c$). However, the layers parallel to the *c*-axis ($\| c$) show the presence of dangling bonds due to the absence of S or M/W atoms at the prismatic edges. 2D layered materials with a large fraction of prismatic edge atoms with unsaturated bonds are inherently unstable in the planar structure and possess high propensity towards curved and closed cage structures. In the present study, we have examined the transformation of the layered structures of the III–IV semiconductors, GaS and GaSe, with indirect bandgaps 3·05 and 2·11 eV, into closed cage structures on exposure to excimer laser irradiation. Hexagonal layered GaS(GaSe) consists of vertically stacked S(Se)–Ga–Ga–S(Se) sheets, in which the interlayers are held together by weak van der Waal interactions and bonding within a layer is predominantly covalent. On the basis of strain energy arguments, it is predicted that both GaS and GaSe layers have the ability to form nanotubes (Cote *et al* 1998; Kohler *et al* 2004). There have been some studies of the formation of nanotubes and fullerene structures of GaS and GaSe (Gautam *et al* 2005; J O Hu *et al* 2005; P A Hu *et al* 2005). We have explained the mechanism of formation of giant onion cage particles from few-layer GaS and GaSe by means of pulsed laser-induced dewetting.

## 2. Experimental

Few-layer GaS and GaSe were prepared by micromechanical cleavage on Si (Late *at al* 2012a,b). The few-layer samples were irradiated under ambient conditions using UV excimer pulsed KrF laser of 248 nm wavelength, 20 ns pulse width and 5 Hz repetition rate. The laser energy was kept constant at 300 mJ and the number of laser pulses was varied from 5 to 50. After laser irradiation, few-layer GaS and GaSe samples were examined by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and Raman spectroscopy. For TEM characterization, the sample after laser irradiation was sonicated in ethanol medium and the well dispersed nanoparticles drop casted on a Cu grid. The thickness of the GaS and GaSe layers was measured using non-contact mode atomic force microscopy (AFM) (Bruker, Innova). FESEM images were obtained using a FEI Nova nanoSEM 600 and TEM images and electron diffraction patterns with a FEI Tecnai $G^2$ S-Twin

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operated at 200 kV using a Gatan CCD camera. Raman spectra were recorded with a 514 nm Ar laser in a Jobin Yvon LabRam HR spectrometer.

## 3. Results and discussion

In figure 1(a) and (b), we show TEM images of few-layer GaS and GaSe with the corresponding electron diffraction patterns as insets. The TEM images clearly indicate the layered structure and the electron diffraction patterns confirm the single crystalline nature with hexagonal symmetry. Figure 2(a) and (b) shows typical AFM images with the corresponding height profiles of few-layer GaS and GaSe. The GaS and GaSe nanosheets contain a few to two layers, the thickness of single layer GaS and GaSe being 0·87 and 0·93 nm respectively.

The response of few-layer GaS and GaSe deposited on Si substrate to UV pulsed laser irradiation was studied using scanning electron microscopy. FESEM images of few-layer GaS recorded as a function of increasing number of laser pulses are shown in figure 3(a)–(d). The starting few-layer GaS shows mica-like morphology as shown in figure 3(a). Pulsed laser irradiation ruptures the surface, forming discrete holes on the surface, after 5 laser pulses (figure 3b). After 10 laser pulses, it initiates dewetting and forms atom of network with a chain-like morphology (figure 3c). Finally, spherical nanoparticles are formed after 50 laser pulses (figure 3d). The response of few-layer GaSe under UV pulsed laser irradiation is similar to that of few-layer GaS as shown on figure 4. Figure 4(a) and (b) shows the FESEM images of as-prepared GaSe and the sample after 50 laser pulses. The average sizes of GaS and GaSe nanoparticles obtained after 50 pulses of laser irradiation are 28 and 30 nm, respectively. The particles show monomodel size distribution and could be fitted with a Gaussian function as shown in figure 4(c) and (d).

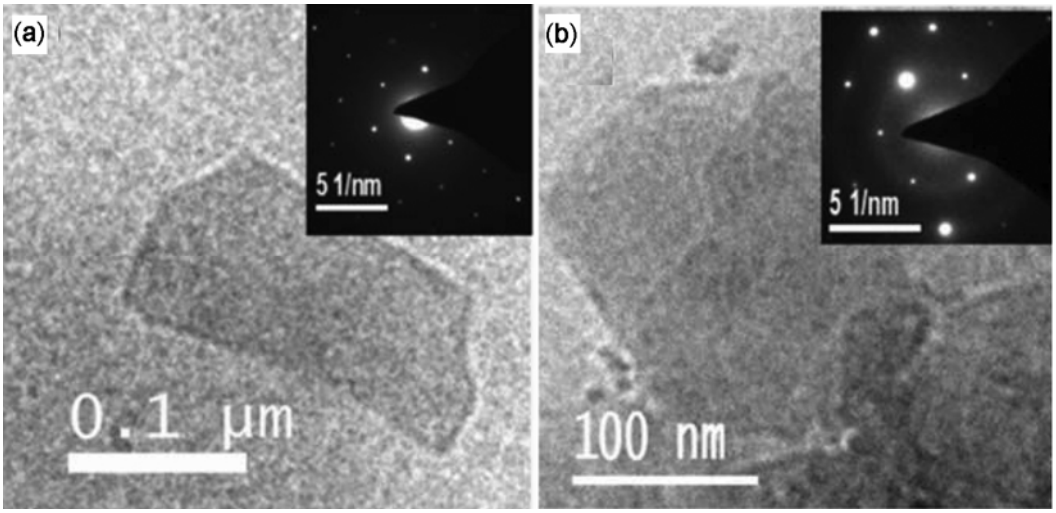


**Figure 1.** TEM images of as-prepared few-layer: (**a**) GaS and (**b**) GaSe with ED patterns as insets.

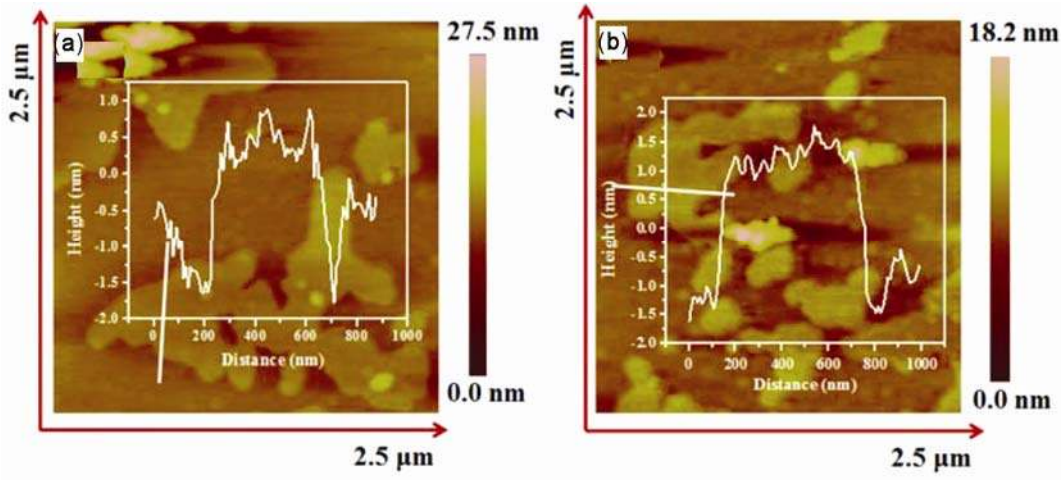


**Figure 2.** AFM images with corresponding height profiles of as-prepared 2-layer: (**a**) GaS and (**b**) GaSe.

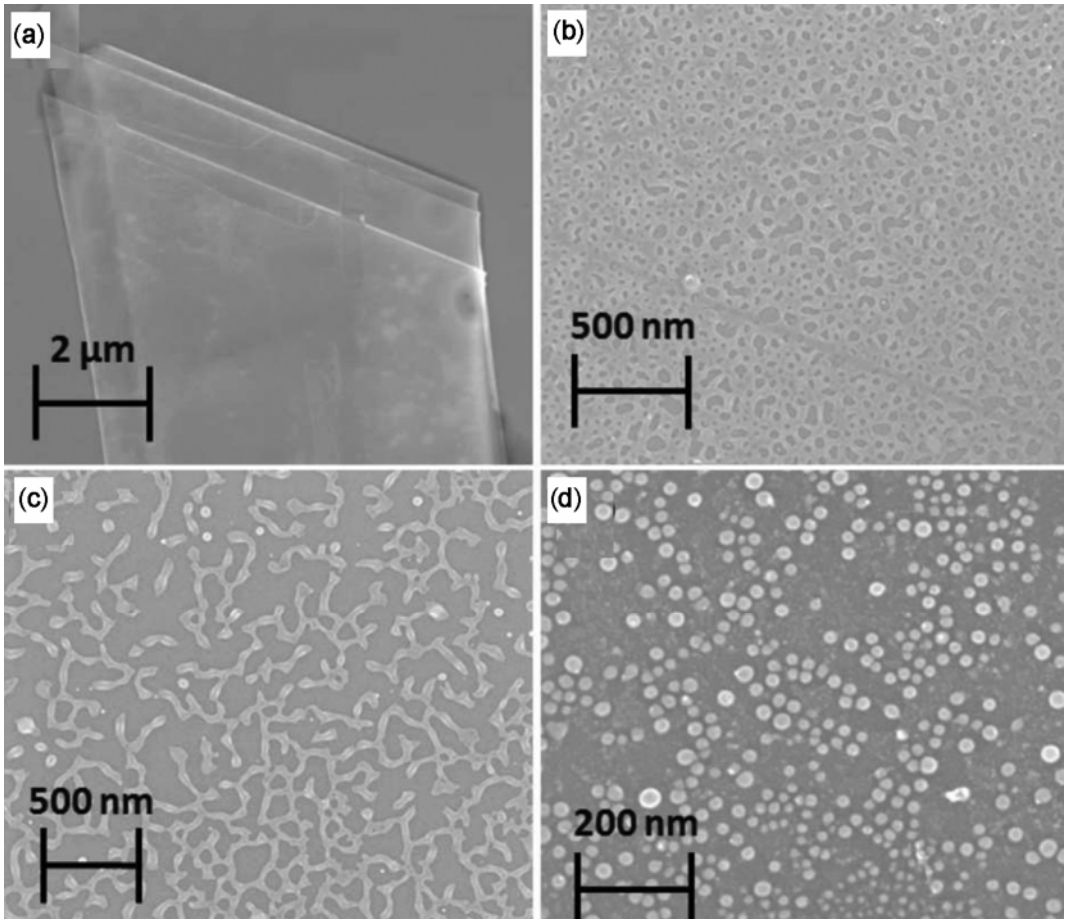


**Figure 3.** FESEM images of few-layer GaS as a function of number of laser pulses: (**a**) as-prepared, (**b**) after 5 layer pulses, (**c**) after 20 layer pulses and (**d**) 50 laser pulses.

In figure 5(a), we show the TEM image of dewetted GaS nanoparticles with the ED pattern as the inset. The particles are polycrystalline and the magnified HREM image (figure 5b) reveals the closed cage giant onion-like structure with about 30–35 concentric layers. We could also see onions with 5–10 (figure 5c) and 2 (inset top panel in figure 5c) concentric layers. The size of the onions varies according to the number of layers as expected. The size of onions with 2 concentric layers is 4 nm, 10 nm with 5–10 layers and ~40 nm with 20–35 layers. From FFT pattern (see inset lower panel in figure 5c) and HREM images, the interlayer spacing is found to be 0·32 nm corresponding to the (1 0 0) planes of GaS. The HREM image of giant GaSe onion-like particle with about 30–35 concentric layers is shown in figure 5(d). Inside this giant onion, we see onion particles with two layers (indicated by arrow). The interlayer spacing of the layer is 0·325 nm corresponding to the (1 0 0) planes of GaSe. The initial thickness of the layers determines the size of the onion cage of GaS and GaSe.

Figure 6(a) shows the comparative Raman spectra of the bulk, few-layer and onion samples of GaS. Single crystal bulk GaS shows three Raman modes in the frequency range 100–400 $cm^{-1}$. The modes are identified as $A^1_{1g}$ (187 $cm^{-1}$), $E^1_{2g}$ (294 $cm^{-1}$) and $A^2_{1g}$ (359 $cm^{-1}$), respectively. The intensity of the $A^1_{1g}$ and $A^2_{1g}$ bands decreases, while that of the $E^1_{2g}$ band increases for few-layer GaS. In the case of the GaS onions, the $A^1_{1g}$ and $A^2_{1g}$ bands disappear and the spectrum exhibits only the $E^1_{2g}$ band. It is observed that in both the few-layer and onion samples, the $E^1_{2g}$ bands shift towards high frequencies (299 $cm^{-1}$). Comparative Raman spectra of the bulk, few-layer and onion of GaSe are shown in figure 6(b). Bulk GaSe shows three intense Raman signals due to the $A^1_{1g}$ (132·2 $cm^{-1}$), $E^1_{2g}$ (211 $cm^{-1}$) and $A^1_{1g}$ (306 $cm^{-1}$) modes and one weak Raman signal due to the $E^2_{1g}$ (251·5 $cm^{-1}$) mode. The intensity of the $A^1_{1g}$ and $A^2_{1g}$ bands decreases while those of the $E^1_{2g}$ and $E^2_{1g}$ bands is negligible in few-layer GaSe. In the onions, the $A^1_{1g}$, $E^1_{2g}$ and $E^2_{1g}$ bands disappear and we can see the $A^2_{1g}$ band with the peak shifted to lower frequencies (299·4 $cm^{-1}$).

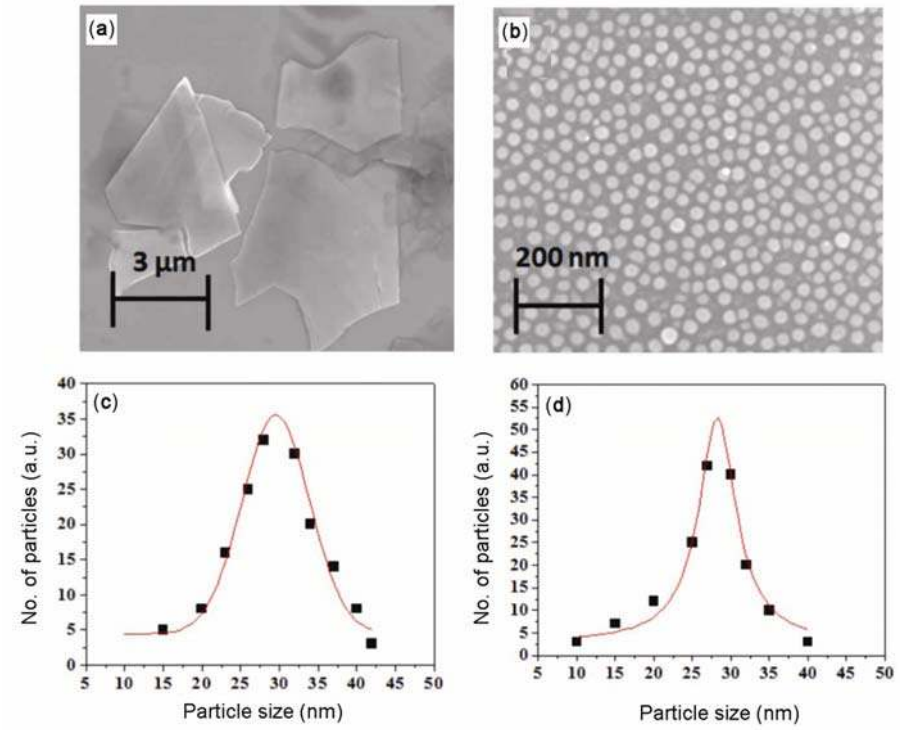


**Figure 4.** FESEM images of few-layer GaSe: (**a**) as-prepared, (**b**) after 50 laser pulses, (**c**) particle size distribution of GaS nanoparticles and (**d**) particle size distribution of GaSe nanoparticles.

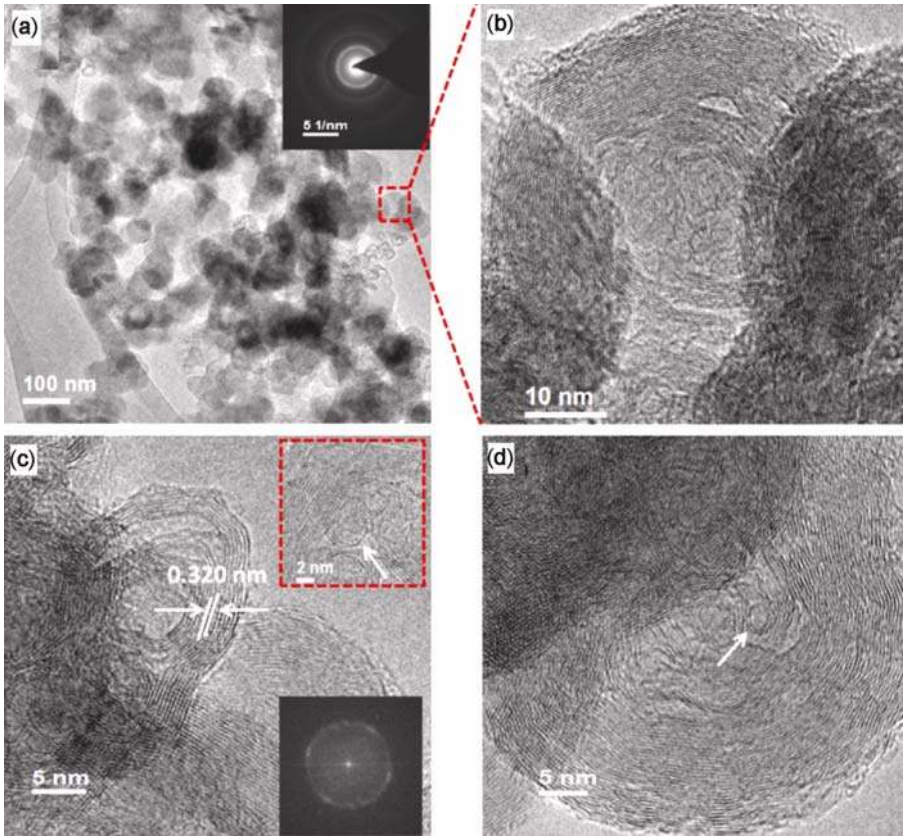


**Figure 5.** (**a**) TEM image of GaS onions with the ED pattern as the inset. (**b**) HREM image of giant GaS onions of 30–35 concentric layers. (**c**) HREM image of GaS onions of 5–10 concentric layers with 2 layer (upper panel) onions, FFT pattern (lower panel) is shown as an inset. (**d**) HREM image of giant GaSe onions of 35–40 concentric layers.

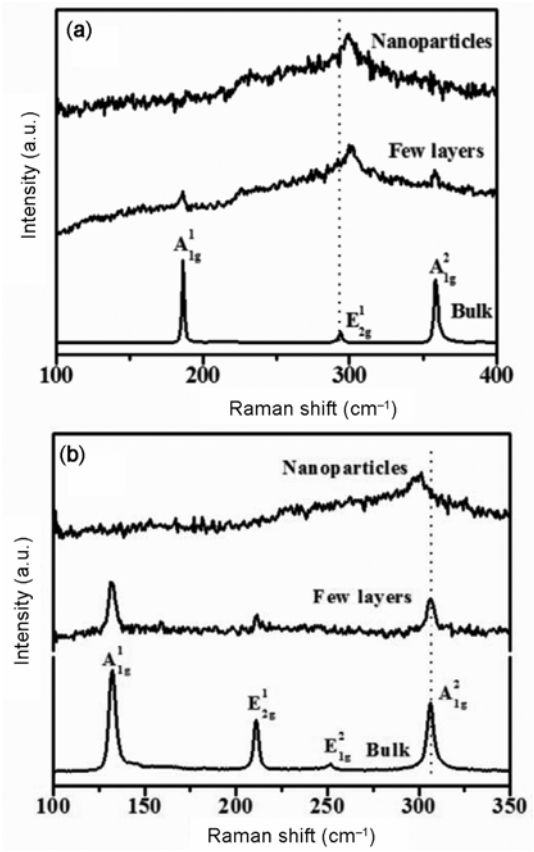


**Figure 6.** Comparative Raman spectra of bulk, few-layer and onions of (**a**) GaS and (**b**) GaSe.

The shifts in the Raman bands of the few-layer samples drawn by us are consistent with early report (Late *et al* 2012).

It has been reported that amorphous carbon and $MoS_2$ nanoparticles spontaneously transform into curved or closed cage crystalline structure on strong electron beam irradiation (Ugarte 1992, 1993; Homyonfer *et al* 1996). An *in situ* aberration-corrected TEM study has shown the direct transformation of a graphene sheet to fullerene, under electron beam irradiation (Chuvilin *et al* 2010). The dewetting is generally treated as a transition from layer to island. In the initial stages of laser irradiation, the holes formed on the surface of few-layers break the bonds between surrounding layers and create more prismatic edges ($\|c$), where reactive dangling bonds exist. By progressively increasing the laser pulses, the dewetting from these edges results in the formation of isolated particles with unsaturated bonds. The weak molecular-substrate interaction at the dewetted edges has more degree of freedom for structural reconstruction. The local laser rapid heating of dewetted edges allowed us to wrap-up and form spheroidal shape of particles with several concentric layers.

## 4. Conclusions

Nanosheets of GaS and GaSe transform from the layered structure into onion cages on exposure to UV excimer pulsed laser irradiation. It appears that dewetting of the few-layer samples creates more prismatic edges and local laser heating at the prismatic edges with unsaturated bonds allows the formation of onions. The diameter of the onions is directly dependent on the number of layers in the starting material.

## Acknowledgements

The author would like to sincerely thank Prof C N R Rao, FRS, for his guidance, constant support and encouragement. He is also thankful to DST, Government of India, for the award of the post-doctoral fellowship for nanoscience and nanotechnology.

## References

Chuvilin A, Kaiser U, Bichoutskaia E, Besley N A and Khlobystov A N 2010 *Nat. Chem.* **2** 450
Cote M, Cohen M and Chadi D J 1998 *Phys. Rev.* **B58** 4277
Gautam U K, Vivekchand S R C, Govindaraj A, Kulkarni G U, Selvi N R and Rao C N R 2005 *J. Am. Chem. Soc.* **127** 3658
Homyonfer M, Mastai Y, Hershfinkel M, Volterra V, Hutchison J L and Tenne R 1996 *J. Am. Chem. Soc.* **118** 7804
Hu J Q, Bando Y, Zhan J H, Liu Z W and Golberg D 2005 *Appl. Phys. Lett.* **87** 153112
Hu P A, Liu Y Q, Fu L, Cao L C and Zhu D B 2005 *Appl. Phys.* **A80** 1413
Kit O O, Tallinen T, Mahadevan L, Timonen J and Koskinen P 2012 *Phys. Rev.* **B85** 085428
Kohler T, Frauenheim T, Hajnal Z and Seifert G 2004 *Phys. Rev.* **B69** 193403
Late D J, Liu B, Luo J, Yan A, Matte H S S R, Grayson M, Rao C N R and Dravid V P 2012a *Adv. Mater.* **24** 3549
Late D J, Liu B, Matte H S S R, Rao C N R and Dravid V P 2012b *Adv. Funct. Mater.* **22** 1894
Lim H E, Miyata Y, Kitaura R, Nishimura Y, Nishimoto Y, Irle S, Warner J H, Kataura H and Shinohara H 2013 *Nat. Commun.* **4** 2548
Nath M and Rao C N R 2001 *J. Am. Chem. Soc.* **123** 4841
Nath M, Govindaraj A and Rao C N R 2001 *Adv. Mater.* **13** 283
Quintana M, Grzelczak M, Spyrou K, Calvaresi M, Bals S, Kooi B, Tendeloo G V, Rudolf P, Zerbetto F and M. Prato 2012 *J. Am. Chem. Soc.* **134** 13310
Rao C N R and Nath M 2003 *Dalton Trans.* 1
Rao C N R, Mueller A and Cheetham A K 2004 *The chemistry of nanomaterials* (Weinheim, Germany: Wiley-VCH)
Tenne R 2006 *Nat. Nanotechnol.* **1** 103
Tenne R and Rao C N R 2004 *Philos. Trans. R. Soc. Lond. A* **362** 2099
Ugarte D 1992 *Nature* **359** 707
Ugarte D 1993 *Chem. Phys. Lett.* **207** 473