Reply to “Comment on ‘Two-Dimensional Boron Monolayer Sheets’”

■ In a recent article,[1] we reported an extensive search of lowest-energy structures of monolayer boron sheets. Among newly predicted lowest-energy boron sheets, three belong to the α-type, namely, $\alpha_1-\alpha_3$, while five belong to the β-type, namely, $\beta_1-\beta_3$, β_6, and β_7. In the latter group, β_4 and β_5 are also named $g_{1/8}$ and $g_{2/15}$, both reported previously by Yakobson and co-workers.[2] Our previous density functional theory (DFT) calculations based on PBE functional and 0.02 $Å^{-1}$ *k*-point space (implemented in the CASTEP 6.0 package[3]) suggest that the α-sheet, first predicted by Tang and Ismail-Beigi,[4] has the greatest cohesive energy, while the cohesive energies of other 10 low-energy sheets are slightly smaller, with their cohesive energy differences being less than a few tens of millielectronvolts (see Table 1 in ref 1). DFT calculations based on the hybrid functional PBE0 with 0.05 $Å^{-1}$ *k*-point space and norm-conserving pseudopotential predicted that α_1- and β_1-sheets have the greatest cohesive energies. In ref 1, we commented that the CATSTEP/PBE0 calculation with the smaller *k*-point space (*e.g.*, 0.02 $Å^{-1}$) is beyond our computing capability (this is because that calculation would require >1 TB computer memory per computer node). Lu *et al.*[5] showed that the PBE0 calculation with 0.02 $Å^{-1}$ *k*-point sampling (comparable to 10 × 10 × 1 *k*-points meshes) is feasible using the VASP 5.2 package and PAW pseudopotential.[6] They found that the cohesive energy of the α-sheet is about 9 meV/atom larger than that of the α_1-sheet. Surprisingly, they also showed an abnormally high peak at the 4 × 4 × 1 *k*-sampling point[5] in the curve of cohesive energy of the α_1-sheet *versus* the *k*-point mesh (see Figure 1A in ref 5). On the basis of this high peak, they pointed out that the cohesive energies computed based on CASTEP 6.0/PBE0 calculation with 0.05 $Å^{-1}$ *k*-point space and norm-conserving pseudopotentials are unreliable.

Since Lu *et al.* used a different program and a different pseudopotential than ours reported in ref 1, we have re-examined the cohesive energies of lowest-energy boron sheets using two hybrid functional implemented in VASP 5.2 program[7] (*i.e.*, HSE06 and PBE0); both are computationally less demanding than the CASTEP/PBE0 computation with a different pseudopotential. Our new computation with the VASP 5.2 program indicates that the abnormally high peak at the 4 × 4 × 1 *k*-sampling point in the curve of cohesive energy of the α_1-sheet *versus* the *k*-point mesh cannot be reproduced, as shown in Figure 1. This high peak is likely an error in Lu *et al.*'s VASP computation.

In addition, as summarized in Table 1, our new VASP/HSE06 and PBE0 calculations predict that $g_{2/15}$-, α-, α_1-, and β_2-sheets are the top-four most stable planar boron sheets due to their cohesive energy differences (≤10 meV). Note that the error bar for the DFT cohesive energy calculation could be as large as 10 meV/atom (functional-dependent). Thus, the VASP/HSE06 and PBE0 calculations support the notion of 2D polymorphous proposed previously.[2]

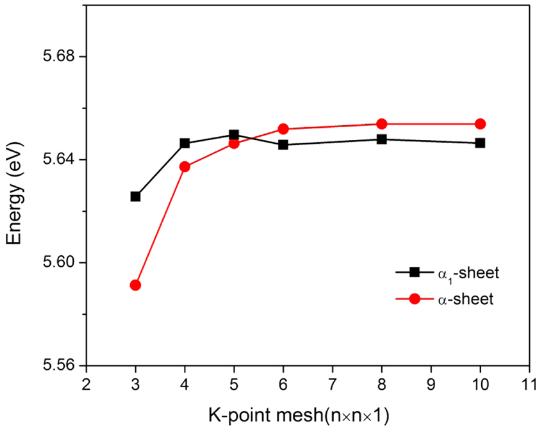

Figure 1. Convergence of cohesive energies of α- and α_1-sheets *versus* the *k*-point mesh based on VASP/PBE0 calculation from this study (this figure is plotted in the same fashion as Figure 1A in ref 5). The cohesive energy difference between the α-sheet and α_1-sheet is less than 9 meV/atom over a wide range of *k*-point mesh. Since the error bar for the DFT cohesive energy calculation can be up to 10 meV/atom, the VASP/PBE0 calculation suggests the α- and α_1-sheets are equally stable.

TABLE 1. Computed Cohesive Energy Per Atom Based on HSE06 and PBE0 Hybrid Functionals, PAW Pseudopotential (All Implemented in VASP 5.2)[a]

boron sheet	α (planar) [α′ (buckled)]	α_1	β_1	β_2	$g_{1/8}$ (β_4)	$g_{2/15}$ (β_5)
E_c(HSE06/VASP) (eV)	**5.692** [5.696]	**5.689**	5.676	**5.687**	5.673	**5.697**
E_c(PBE0/VASP) (eV)	**5.654** [5.659]	**5.646**	5.634	**5.646**	5.632	**5.656**

[a] Here, the 0.02 $Å^{-1}$ *k*-point sampling and 20 Å vacuum space are used. The cohesive energy differences among four most stable planar boron sheets are within 10 meV (values in bold).

In conclusion, (1) Lu *et al.*'s conclusion and comment is mainly based on a different program and a different pseudopotential from those reported in ref 1. (2) Their reported abnormally high peak in the curve of cohesive energy of the α_1-sheet *versus* the *k*-point mesh cannot be reproduced by us. (3) Our new DFT calculations with two hybrid functionals, PBE0 and HSE06 (both implemented in VASP 5.2 program), suggest that (at least) four planar boron sheets, namely, $g_{2/15}$-, α-, α_1-, and β_2-sheets, are equally stable as their cohesive energy differences (≤10 meV). (4) Because the buckled α′-sheet is more stable than the planar α-sheet (Table 1), the α_1-sheet is still the most stable planar sheet of the α-type, while the $g_{2/15}$- and β_2-sheets are the most stable planar sheets of the β-type. However, in view of the functional and pseudopotential dependence on the predicted relative stabilities of several boron sheets (see Table 1 in ref 1 and Table 1 in this text), one must await high-resolution TEM measurement of the atomic structures of boron sheets or single-walled boron nanotubes to resolve whether some of these boron sheets (polymorphs) can be equally stable or coexist.

Note in passing that the main motivation for us to use the hybrid functional PBE0 in ref 1 is to examine whether the lowest-energy boron sheets are metallic or semiconducting, in light of the fact that the PBE/GGA functional tends to underestimate the band gap. In ref 1, we report that the planar α-sheet and buckled α′-sheet are semiconducting based on the PBE0 calculation, whereas all other lowest-energy boron sheets considered are metallic. This conclusion will be useful to experimentalists for detecting electronic properties of boron sheets if monolayer boron sheets were isolated.

REFERENCES AND NOTES

1. Wu, X. J.; Dai, J.; Zhao, Y.; Zhuo, Z. W.; Yang, J. L.; Zeng, X. C. Two-Dimensional Boron Monolayer Sheets. *ACS Nano* **2012**, *6*, 7443–7453.
2. Penev, E. S.; Bhowmick, S.; Sadrzadeh, A.; Yakobson, B. I. Polymorphism of Two-Dimensional Boron. *Nano Lett.* **2012**, *12*, 2441–2445.
3. Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. J.; Refson, H.; Payne, M. C. First Principles Methods Using CASTEP. *Z. Kristallogr.* **2005**, *220*, 567–570.
4. Tang, H.; Ismail-Beigi, S. Novel Precursors for Boron Nanotubes: The Competition of Two-Center and Three-Center Bonding in Boron Sheets. *Phys. Rev. Lett.* **2007**, *99*, 115501.
5. Lu, H. G.; Mu, Y. W.; Li, S. D. Comment on "Two-Dimensional Boron Monolayer Sheets". *ACS Nano* **2013**, 10.1021/nn3033562.
6. Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. *J. Chem. Phys.* **1999**, *110*, 6158.
7. Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Erratum: "Hybrid Functionals Based on a Screened Coulomb Potential". *J. Chem. Phys.* **2006**, *124*, 219906.

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Received for review December 25, 2012

10.1021/nn305981j