



## Research paper

## Fullerene-based low-density superhard materials with tunable bandgaps

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## ABSTRACT

Four carbon allotropes built from tetrahedral symmetrical fullerenes  $C_{28}$  and  $C_{40}$  are predicted to be superhard materials with mass density around that of water, and all of them are porous semiconductors. Both the bandgaps and hardness decrease with increasing ratio of  $sp^2$  hybridized carbon atoms. The mechanical and thermodynamic stabilities of  $C_{28}$ - and  $C_{40}$ -based allotropes at zero pressure are confirmed by a variety of state-of-the-art theoretical calculations. The evolution trend of bandgap found here suggests that one can obtain low-density hard materials with tunable bandgaps by substituting the carbon atom in diamond with different  $T_d$ -symmetrical non-IPR fullerene  $C_n$ .

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Elemental carbon can form a large number of allotropes including graphite, diamond, fullerenes, carbon nanotubes and graphene et al. Recent years, many new carbon allotropes with excellent hardness have been predicted and characterized [1–8]. Although the microscopic mechanism of hardness is not understood well, it is a consensus that it should be the short and strong C–C bond make diamond a superhard material [9]. Actually cubic BN materials formed by strong B–N bond with similar space stacking mode and comparable density to diamond has been found to be also superhard [10,11]. To a large extent, diamond has been a structural template for building superhard materials [12–14]. However, the densities of diamond, cubic BN and other experimentally reported diamond-like analogues are all near to  $3.5 \text{ g}\cdot\text{cm}^{-3}$ . Transition metal-based superhard materials have much higher mass density, however, generally lower hardness [15–19]. Thus, it is significant to answer if there is a superhard materials with much lower mass density than diamond for both fundamental research and practical applications.

For low-density superhard materials, the atomic weight of its each component element should be as small as possible and each atom is desired to form  $sp^3$  hybridized bonds so that a high-strength three dimensional network can be formed. Thus, the candidate elements are likely limited to B, C and N. In fact, BN superhard materials can be thought as an analogue of diamond, thus for searching a low-density superhard materials, the candidate element can be initially limited to carbon, and the structural template may be initially limited to diamond.

In fact, some theoretical progress has been achieved in searching low-density hard or superhard materials based on diamond. T-carbon was predicted to have a Vickers hardness of 61.1 GPa with a density of only  $1.50 \text{ g}\cdot\text{cm}^{-3}$  [4].  $C_{96}$  carbon was predicted to have a Vickers hardness of 32 GPa with a low mass density ( $2.7 \text{ g}\cdot\text{cm}^{-3}$ ) [5].  $C_{20}$ -T carbon was predicted to have Vickers hardness of 72.76 GPa with a mass density of  $3.298 \text{ g}\cdot\text{cm}^{-3}$  [6].  $C_{14}$ -diamond was predicted to have Vickers hardness of 55.8 GPa with a mass density of  $3.37 \text{ g}\cdot\text{cm}^{-3}$  [20]. These theoretical findings put some insight into the nature of hardness, and some of them can rationalize the corresponding experimental observations. However, little attention has been paid on their building blocks and thus neglect the question if it is possible to form these allotropes.

Here, we designed allotropes with low-energy fullerene isomers as building blocks. It is impossible to directly form networked high-strength materials for carbon nanotubes and grapheme since the intermolecular interaction is undoubtedly much weaker than that of intramolecular covalent interaction. However, carbon atoms at the fused pentagons of a non-IPR fullerene [21] is highly reactive and can form strong intermolecular covalent bond. Thus it is possible to form a high-strength allotrope from non-IPR fullerenes. Actually, both  $T_d$ - $C_{28}$  and  $T_d$ - $C_{40}$  fullerenes are low-energy isomers and have been detected in mass spectrum experiments of the soot for producing fullerenes or metallofullerenes. They can be considered as superatoms with four unpaired electrons distributed in the four  $V_{555}$  (the vertex intersected by three adjacent pentagons) and thus are ideal candidate building blocks to form three dimensional network with strong intermolecular covalent bonds.

We obtained cubic and hexagonal diamond-like structures of  $T_d$ - $C_{28}$  and  $T_d$ - $C_{40}$  fullerenes and examined the mechanical and

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thermodynamic stabilities of these new carbon phases by density functional theory calculations. The calculations reveal that  $C_{28}$ - and  $C_{40}$ -based diamond-like structures are superhard semiconductors with mass density near to or lower than that of water. The microscopic mechanism of hardness, structural and mechanical stability, electronic band structures of them are discussed in detail.

The optimized cells of diamond-like allotropes from  $T_d-C_4$ ,  $T_d-C_{28}$ , and  $T_d-C_{40}$  are shown in Fig. 1, the calculated lattice parameters and density are list in Table 1. The total energy per atom (TEPA) against its volume for the considered allotropes of carbon are shown in Fig. 2.

Table 1 shows that the lattice parameters of cubic (3.57 Å) and hexagonal (2.51 and 4.17 Å), diamond are in good agreement with experimental values of cubic (3.57 Å) and hexagonal (2.52 and 4.12 Å) diamond; meanwhile, the lattice parameter of cubic  $T_d-C_4$  allotrope (7.52 Å) is the same to theoretical value of T-carbon [4]. These results demonstrate that the employed computational method is suitable for our system.

Fig. 2 shows that the TEPA of each optimized structure is minimum for all these allotropes, indicating they are thermodynamically stable. At the same time, it is shown that graphite has the lowest minimum TEPA, which is consistent with recent theoretical results [5]. The TEPA of  $C_{28}$ - and  $C_{40}$ -based allotropes are a little higher than those of diamond and graphite, indicating that they are thermodynamically metastable phases against diamond and graphite. However, the TEPA of them are much lower than that of T-Carbon (cubic  $C_4$ ), indicating they are energetically more favored than T-carbon. The volume per atom of  $C_{28}$ - and  $C_{40}$ -based allotropes are smallest for all considered allotropes, so their density are smallest among all considered carbon allotropes.

To confirm the structural stability of the these allotropes, we calculated the phonon dispersion of at ambient pressure. As shown in Fig. 3, no imaginary frequencies are observed throughout the entire Brillouin zone of the these allotropes, confirming their dynamic stabilities. The calculated highest phonon frequencies of C–C bond stretching mode in these allotropes are around 45THz,

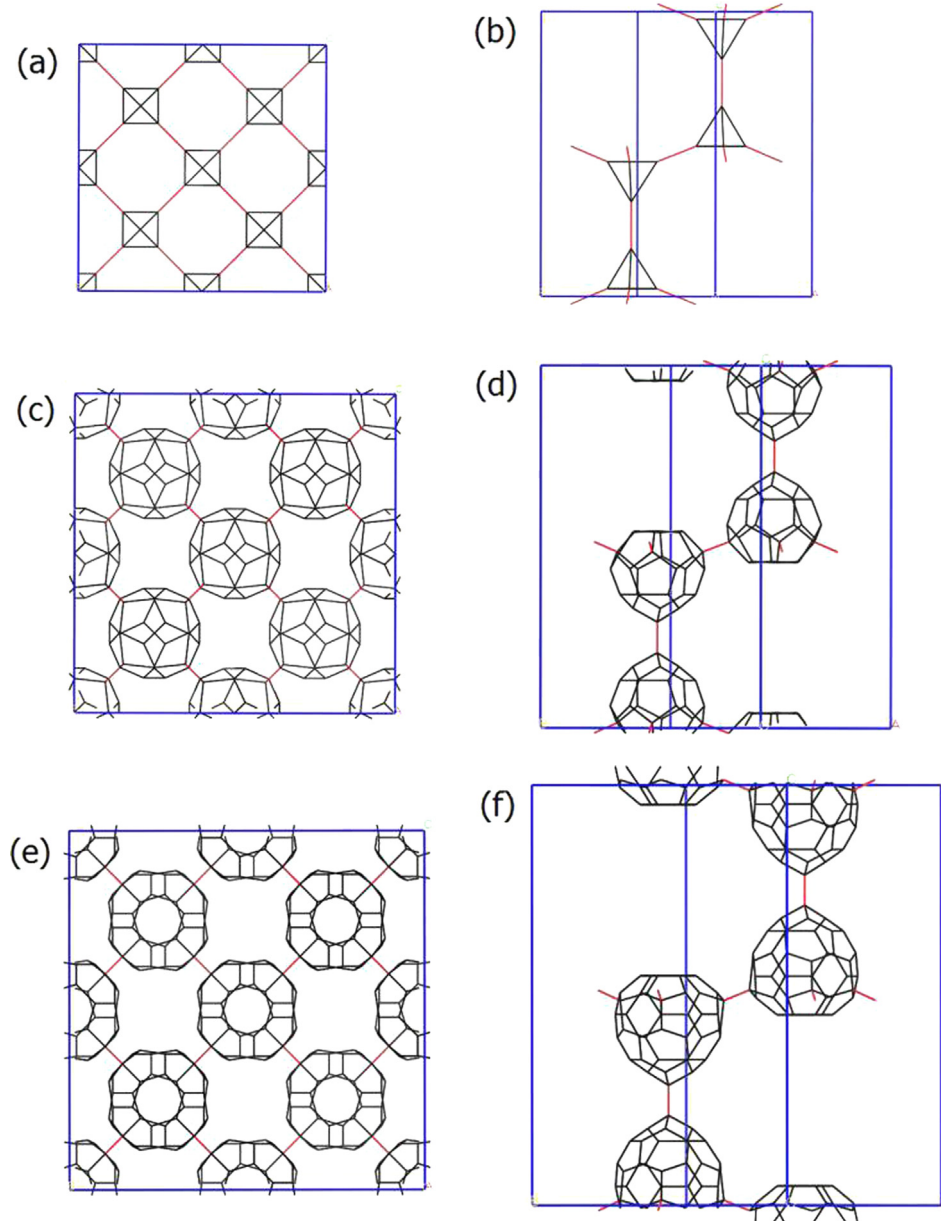


Fig. 1. The cells of diamond-like allotropes from  $T_d-C_4$ ,  $T_d-C_{28}$ , and  $T_d-C_{40}$ .

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