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Varying Topological Properties of Two-Dimensional Honeycomb Lattices Composed of Endohedral Fullerenes

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Honeycomb lattices (HLs) have been widely explored for realization of massless Dirac quasiparticles and intriguing topological properties in both the quantum and classical regimes, with elemental and artificial atoms as the corresponding building blocks. Here we provide the first demonstration that when the fullerene molecules of C_{28} are used as the prototypical building blocks, stable two-dimensional (2D) HLs can also be achieved, with the structural, electronic, and topological properties tuned via proper atom encapsulation. Specifically, whereas a closely packed structure is preferred for the C_{28} lattice, honeycomb structures with different spacial symmetries are energetically favored for both the $Bi@C_{28}$ and $In@C_{28}$ endohedral fullerenes. In particular, $Bi@C_{28}$ -HL is revealed to be a quantum spin Hall insulator because of strong spin-orbit coupling effects in the f molecular orbitals, while $In@C_{28}$ -HL is a quantum valley Hall insulator as the result of mirror symmetry breaking. The present study offers superatom-based new platforms for realizing quantum spin Hall and quantum valley Hall effects in 2D systems, with distinctly enhanced tunability and robustness against atomic-scale imperfections.

In two-dimensional (2D) materials, honeycomb lattice (HL) is the most common crystal structure that can harbor Dirac electrons with linear dispersion, thereby occupying the central platform for realization of various topological states [1, 2]. Graphene is a representative 2D material with carbon atoms arranged on the HL. The demonstration of exfoliated graphene [3] has stimulated substantial efforts to make the system topologically nontrivial. Earlier theoretical studies have shown that graphene can be converted into a quantum spin Hall insulator or quantum valley Hall insulator by introducing sufficiently strong spin-orbit coupling (SOC) [4–7] into the system or breaking its sublattice symmetry [1, 8–12]. However, experimental realizations of these topological electronic states in graphene-based systems have met various standing challenges. One is well known: the SOC is too weak in these systems [13]. Another challenge is more subtle: it is difficult to achieve controlled geometric boundaries with atomic precision, which is otherwise essential for engineering and observing various topological edge states [14].

Beyond pristine graphene, other types of materials possessing graphene-like HLs have also been extensively explored [6, 7]. Here, one appealing line of research is to replace the elemental atoms by diatomic molecules such as CO [15], superatoms such as fullerenes [16], and artificial atoms such as nano-, micro-, or even macro-sized clusters as the building blocks [14, 17–21]. For the latter systems residing in the classical regime, including sonic crystals [14, 17], photonic crystals [18, 19], and other artificial metamaterials [20, 21], both the Dirac quasipar-

ticles and topological states have been realized. For the former systems focusing on the electronic properties in the quantum regime, the Dirac nature of the fermions has also been observed (for the CO based HL) or predicted (for the fullerene based HL); yet to date, definitive observations of topologically nontrivial quantum states of artificial HLs are still lacking.

In this Letter, we investigate 2D molecular lattices composed of fullerenes as potential new platforms to harbor topologically nontrivial electronic states. Here, the different types of encapsulated atoms and rotational degrees of freedom of the building blocks can be exploited to tune the structural, electronic, and topological properties of the molecular crystals, as demonstrated by our first-principles calculations. We show that, whereas a closely packed structure is preferred for the pure C_{28} lattice, honeycomb structures with different spacial symmetries are favored for both the $Bi@C_{28}$ and $In@C_{28}$ endohedral fullerenes. These two systems also possess distinct Dirac bands derived from f molecular orbitals, and energy gaps in these bands can further be opened via different mechanisms: stronger spin-orbit coupling in the former due to heavier encapsulated atoms, and mirror symmetry breaking in the latter due to molecular rotations. We also show that $Bi@C_{28}$ -HL is a quantum spin Hall insulator, while $In@C_{28}$ -HL is a quantum valley Hall insulator. Furthermore, well-defined grain boundaries between topologically nonequivalent domains can be fabricated by rotating the C_{28} molecules or changing the encapsulated atoms without introducing atomic defects, thereby offering new plausibilities for experimental

FIG. 1. (a)-(c) Top views (upper panels) and side views (lower panels) of 2D lattice structures consisting of pure C_{28} molecules. (a) Closely packed structure, (b)-(c) HLs with C_{3v} and C_3 symmetry, respectively. (d)-(f) are the corresponding electronic band structures. The two sublattices in the HLs are labelled by A and B. The dashed line in (b) denotes a mirror symmetry in the direction normal to the 2D plane. The arched arrow in (c) indicates the rotation of the C_{28} molecule on the A sublattice site. Molecules on different sublattices are distinguished by different colors when the mirror symmetry is broken. The blue dashed lines in (e) represent the first BZ, in which the band structures are plotted along the blue solid lines. The two Dirac points (DPs) in (e) are also indicated. The Fermi energies are set to be zero.

realization of quantum spin/valley Hall effects and topologically protected edge states based on 2D molecular crystals.

Our first-principles density functional theory (DFT) calculations were carried out in the framework of the recently developed strongly constrained and appropriately normed (SCAN) meta-generalized gradient approximation for short- and intermediate-range interactions [22] as implemented in the Vienna *ab initio* simulation package (VASP) [23]. For the systems considered in the present study, our test runs show that there is no obvious difference between the calculated results from the SCAN scheme and the SCAN+rVV10 scheme, the latter has considered long-range van der Waals (vdW) interactions [24]. We therefore only present the SCAN results in the rest of this paper. All the self-consistent calculations were performed with a plane-wave cutoff of 400 eV, and the Brillouin zone (BZ) was sampled by a $7 \times 7 \times 1$ or $1 \times 7 \times 1$ k -mesh. Supercells with a vacuum layer more than 15 Å in thickness were used to ensure decoupling between neighboring slabs. For structural relaxation, all the atoms were allowed to relax until the atomic forces are smaller than 0.003 eV/Å. Phonon spectra were obtained using the PHONOPY code [25, 26]. The DFT results were adopted as inputs to construct the maximally localized Wannier functions (MLWFs), using the WANNIER90 code to calculate the Berry curvature and topo-

TABLE I. Lattice constants a_0 and binding energies E_b of pure C_{28} , Bi@ C_{28} , and In@ C_{28} molecular crystals with different lattice structures. The Bi@ C_{28} -HL- C_3 structure is absent because it would collapse upon structural relaxation.

	C_{28}		Bi@ C_{28}		In@ C_{28}	
	a_0 (Å)	E_b (eV)	a_0 (Å)	E_b (eV)	a_0 (Å)	E_b (eV)
Closely packed	6.63	-3.50	6.76	-0.04	6.76	-0.44
HL- C_{3v}	11.08	-3.21	11.26	-2.02	11.43	-2.21
HL- C_3	11.15	-3.37	—	—	11.26	-2.26

logical invariants [27].

A fullerene molecule C_n generally contains n carbon atoms that form a hollow sphere or other geometric shapes. Here we focus on C_{28} , which possesses a spherical shape and belongs to the point group C_{3v} . In sharp contrast to C_{60} , which prefers a vdW solid, C_{28} molecules are expected to form a covalent crystal [28]. Figures 1(a)-(c) show the lattice structures of three candidate types of 2D covalent crystals composed of C_{28} , with the corresponding electronic structures shown in Figs. 1(d)-(f). While the closely packed structure is a trivial insulator [Fig. 1(d)], the C_{28} -HL- C_{3v} structure harbors Dirac electrons at ~ 1 eV above the Fermi level [Figs. 1(e)]. Furthermore, when the mirror symmetry is broken [Fig. 1(c)], the system develop band gaps in the Dirac cones [Fig. 1(f)]. From the binding energy comparisons in Table I, we see that the closely packed structure is clearly favored, despite the observations that the other two structures possess more intriguing electronic properties. Here the binding energy is defined by $E_b = E_{2D}/m - E_{mol}$, where E_{2D} is the energy of the 2D crystal per unit cell, m is the number of C_{28} molecules in one unit cell, and E_{mol} is the energy of an isolated C_{28} molecule.

Our next objectives are to stabilize the C_{28} -HL- C_{3v} and C_{28} -HL- C_3 via proper atom encapsulation. Earlier studies have shown that the hollow structure of C_{28} is able to encapsulate atoms inside, namely endohedral fullerene [29–32]. In the present study, the choices of Bi and In atoms are based on the observations that the encapsulation of either type of atoms is able to stabilize the HL structure over the closely packed structure, as shown by our detailed calculations. Furthermore, the strong SOC associated with the Bi atoms is highly desirable for realizing topological properties. The lattice constants a_0 and binding energies E_b of the different 2D molecular crystals are compared in Table I. The Bi@ C_{28} and In@ C_{28} systems prefer the HL structures with C_{3v} and C_3 symmetry, respectively, as shown in Figs. 2(a) and (b). We have also calculated the phonon spectra of the energetically stable structures to confirm their dynamic stability (see Supplemental Material [33] for the phonon spectra), and have ruled out the unstable Bi@ C_{28} -HL- C_3

structure.

Given the established structural and energetic stabilities of $\text{Bi@C}_{28}\text{-HL-}C_{3v}$ and $\text{In@C}_{28}\text{-HL-}C_3$, we next investigate their topological properties in turn. As implicitly expected from Fig. 1(e), and explicitly illustrated in Fig. 2(c), the band structure of $\text{Bi@C}_{28}\text{-HL-}C_{3v}$ possesses distinct Dirac cones around the BZ corners of $K_{1,2}$. Beyond this observation, there exist two additional important aspects. The first is the upward shifting of the Fermi level to coincide with the Dirac point upon Bi encapsulation, which is highly desirable to the realization of its potential topological properties. The corresponding charge transfer deduced from the shifting is 3 electrons per Bi atom. Secondly, since the atomic SOC of Bi is strong, the Bi encapsulation also results in a band gap opening of ~ 6 meV at the Dirac point. In close analogy to the original Kane-Mele model of graphene (but there with the assumption of an unphysically large SOC) [4], here the induced band gap by the physically realistic SOC could convert the system into a quantum spin Hall insulator.

Here, the artificial frontier molecular orbitals (MOs) of Bi@C_{28} are f orbitals [16, 34]. When Bi@C_{28} molecules are arranged into a honeycomb lattice, these f MOs split. Based on our VASP calculations and WANNIER90 code [27] fittings, the highest occupied MO and lowest unoccupied MOs in the $\text{Bi@C}_{28}\text{-HL-}C_{3v}$ superlattices are $f_{y(3x^2-y^2)}$ orbitals with $j = 3 \pm 1/2$ (see Fig. S2 [33]). The Dirac bands formed by the $f_{y(3x^2-y^2)}$ orbitals open relatively large band gaps, when the Bi atom induces strong SOC effects into this system. To quantitatively verify the topological nature of $\text{Bi@C}_{28}\text{-HL-}C_{3v}$, we have adopted the WANNIER90 code combined with VASP to calculate the Berry curvature and corresponding topological invariant. We obtain $\mathbb{Z}_2=1$, which unambiguously characterizes $\text{Bi@C}_{28}\text{-HL-}C_{3v}$ to be a quantum spin Hall insulator. It is also noted that the slight splitting in the valence bands shown in the inset of Fig. 2(c) arises from the Rashba SOC effect associated with the inversion symmetry breaking of the 2D molecular crystals [see the side views in Figs. 1(a)-(c)].

Beyond the 2D bulk properties, we should also expect the presence of symmetry-protected boundary states in finite systems following the bulk-boundary correspondence [35]. For this purpose, we have calculated the band structure of a $\text{Bi@C}_{28}\text{-HL-}C_{3v}$ nanoribbon with zigzag edges. As shown in Fig. 3(a), the lateral width of the nanoribbon contains $N = 16$ molecules to safely eliminate potential finite size effects. Figures 3(b) and (c) display the band structures, where the topological edge states are easily identified. Furthermore, each band around the X point splits into two sub-bands, with the corresponding electrons in the sub-bands located at the two opposite edges of the ribbon as shown in Fig. 3(a). The energy splitting between the edge states is again attributed to the inversion symmetry breaking and the cor-

FIG. 2. Stable crystal structures of (a) $\text{Bi@C}_{28}\text{-HL-}C_{3v}$ and (b) $\text{In@C}_{28}\text{-HL-}C_3$, where the solid rhombuses denote the unit cells and the horizontal dashed line in (a) indicates the mirror symmetry in the direction normal to the 2D plane. (c) Band structure and atom-projected density of states (PDOS) of $\text{Bi@C}_{28}\text{-HL-}C_{3v}$ with SOC. The inset highlights the gap opening and band splittings associated with the stronger intrinsic SOC of Bi and Rashba SOC of the lattice. (d) Band structure of $\text{In@C}_{28}\text{-HL-}C_3$ and real-space charge distributions of the valence and conduction valleys at the Γ point. The isosurface is plotted at $0.003 e/\text{\AA}^3$, where yellow depicts positive and green negative sign of the wave functions. The inset in (d) illustrates the sharply peaked and highly localized Berry curvature within a given valley. The Fermi level is set to be zero, as indicated by the horizontal green dashed lines in (c) and (d).

responding Rashba SOC effect. Our first-principles calculations show that the edge states of the $\text{Bi@C}_{28}\text{-HL-}C_{3v}$ nanoribbon around the Fermi level are intact with or without hydrogen passivation on the edge molecules, as such passivation only affects the electronic bands far away from the topological edge states. It indicates that the MO-based topological states are inherently more robust against localized or atomic-scale imperfections within the systems.

Now we move to the topological properties of the $\text{In@C}_{28}\text{-HL-}C_3$ system. For this system, as shown in Figs. 2(b) and (d), a band gap of ~ 88 meV appears as the results of both the inversion and mirror symmetry breaking, making the two valleys at the $K_{1,2}$ points inequivalent. The encapsulation of In atoms also shifts the Fermi level into the Dirac bands, corresponding to a net charge transfer of 3 electrons per In atom making the Fermi level shift to the Dirac-like bands of $f_{y(3x^2-y^2)}$ MOs. The real-space charge distributions of both the bonding and anti-bonding $f_{y(3x^2-y^2)}$ MOs are shown in the right panel of Fig. 2(d), showing that all the atoms of the fullerene molecule contribute comparably to the valley states. Previous studies based on graphene-like systems had shown that the two valleys in the HJs can act as binary pseudospins and harbor valley-based topo-

FIG. 3. (a) Top view of a $\text{Bi}@C_{28}\text{-HL-}C_{3v}$ zigzag nanoribbon and charge distribution of the topological edge states around the X point marked as ESU and ESD in (c). The projections along the x axis are renormalized and plotted by the red curves below. The isosurface is plotted at $0.003 e/\text{\AA}^3$. The lateral width of the nanoribbon is $N = 16$ molecules. (b) Band structure of the $\text{Bi}@C_{28}\text{-HL-}C_{3v}$ nanoribbon. (c) The zoom-in bands around the Fermi level. Each band splits into two sub-bands marked as ESU and ESD. The red curves in (b) and (c) are the topological edge states.

logical states known as the quantum valley Hall effect in the absence of short-range scattering events [8–12, 36–38]. On a quantitative level, we can confirm that the $\text{In}@C_{28}\text{-HL-}C_3$ system is indeed an intrinsic and topologically nontrivial quantum valley Hall insulator. As shown in the inset of Fig. 2(d), the Berry curvatures of the occupied bands are primarily localized around the K_1 and K_2 valleys with the same magnitude but opposite signs. The calculated Chern numbers are $\mathcal{C}_{k_1} = +0.92$ and $\mathcal{C}_{k_2} = -0.92$ at the two different valleys, close to the ideal integers of ± 1 [1, 2, 39].

Similar to the $\mathbb{Z}_2$ topological insulator of $\text{Bi}@C_{28}\text{-HL-}C_{3v}$, the topological nature of the quantum valley Hall insulator of $\text{In}@C_{28}\text{-HL-}C_3$ can also be manifested by its unique edge states, which is robust in the absence of short-range scatterings. Previous model studies based on the monolayer HL predicted that there are insulating edge states in a single zigzag nanoribbon and metallic edge states at the heterojunction of two topologically nonequivalent zigzag nanoribbons [1, 40]. Here we construct a single zigzag nanoribbon with the width $N = 16$ molecules and a heterojunction consisting of two such nanoribbons as shown in Figs. 4(a) and (b), respectively. The heterojunction is designed by inverting the rotation angle of the molecules on the A and B sublattice sites,

FIG. 4. (a) Top view of a $\text{In}@C_{28}\text{-HL-}C_3$ nanoribbon with width of $N = 16$ molecules. (b) Top view of a heterojunction of two $\text{In}@C_{28}\text{-HL-}C_3$ nanoribbons and charge distribution of the topological edge states around the X point as marked in (d). The projection along the x axis is renormalized and plotted by the red curve below. The isosurface is plotted at $0.003 e/\text{\AA}^3$. The black dashed line indicates the grain boundary along the y axis. (c) Band structure of the insulating ribbon shown in (a). (d) Band structure of the metallic heterojunction shown in (b). The red curves in (c) and (d) are the valley-based topological edge states.

namely, the A/B sublattices are exchanged in the two nanoribbons. The molecules on the A and B sublattice sites are marked with different colors in Fig. 4(b), with A-A bonds lying along the grain boundary. Specifically, the heterojunction can be formed via tuning the internal degrees of freedom of the fullerene molecules without introducing atomic defects at the heterojunction. Figure 4(c) shows the band structure of the single zigzag nanoribbon, where the edge states do not cross the Fermi level within the gap of ~ 10 meV. The edge states are nearly flat around the X point. The weak dispersion can be attributed to the electron correlation effect in the system, weak but non-negligible finite size effect, and/or other electronic interactions. Figure 4(d) shows the band structure of the heterojunction, where the edge states cross the Fermi level at both K_1 and K_2 points. Figure 4(b) shows the corresponding real-space charge distribution of the edge states at the X points, showing that these states are mainly localized at the interface of the heterojunction.

Before closing, we discuss some generic or practical aspects of the ideas presented in this study. First, we showed that the fullerene molecules acting as superatoms can be stabilized in superlattice for exploiting 2D topological phases. The topological edge states associated with the MOs are expected to be also more robust than the atomic orbitals in the presence of atomic defects, es-

pecially when the electronic states from the atomic defects are far away. Future studies are expected to expand the approach to other types of molecules or fullerenes. Secondly, the recent successes in the fabrication of various nanostructures using self-assembly or other types of bottom-up approaches serve as ensuring factors that the proposed $\text{Bi@C}_{28}\text{-HL-}C_{3v}$ and $\text{In@C}_{28}\text{-HL-}C_3$ systems can be eventually realized experimentally on proper substrates, especially given the observations that these 2D structures are energetically favored and are also dynamically stable. As some compelling examples, graphene nanoribbons and superlattices have been predicted and fabricated very recently using proper molecular precursors, resulting in topologically nontrivial phases and robust edge states [41–43]. Thirdly, a definitive observation of accurately quantized plateaus of the quantum spin Hall effect is still lacking [44–47], especially in samples with large sizes, and the underlying reason has been mainly attributed to effects and noises from the inevitable existence of dangling bonds and defects [47, 48]. The lack of dangling bonds and atomic-scale defects in the nanoribbons and heterojunctions based on the fullerene crystals is naturally beneficial to experimental realization of the quantum spin Hall effect, quantum valley Hall effect, and in particular the existence of the corresponding topologically protected edge states of such 2D systems [33, 48].

In summary, we have demonstrated that 2D fullerene crystals can now be added as new members of the topological materials family. When compared with the 2D atomic crystals such as graphene, the structural, electronic, and topological properties of such molecular crystals can be more readily tuned by encapsulating different functional atoms into the fullerene molecules and/or by rotating the molecules on the sublattice sites of the honeycomb structure. As prototypical examples, we have shown that the $\text{Bi@C}_{28}\text{-HL-}C_{3v}$ and $\text{In@C}_{28}\text{-HL-}C_3$ are respectively $\mathbb{Z}_2$ topological insulator and valley-based topological insulator. The present study offers appealing new platforms for realizing quantum spin Hall and quantum valley Hall effects in 2D molecular crystals.

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