Obtaining Intrinsically Occupied Free-Space Superatom States in an Encapsulated Ca$_2$N Nanotube

Ghulam Abbas,* Songtao Zhao, Zhenyu Li,* and Jinlong Yang*

Hefei National Laboratory for Physical Sciences at the Microscale, Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

ABSTRACT: By considering a group of atoms as a whole, the superatom state concept has been proposed to understand complex chemical systems. Superatom states distributed in free space are important in determining the interactions between superatoms and also the reaction of a superatom system with other external molecules. Unfortunately, all free-space superatom states reported to date are unoccupied states, which strongly limit their applications. In this study, we predict that both occupied and unoccupied free-space superatom states exist in an encapsulated Ca$_2$N nanotube. In this composite system, the inner Ca$_2$N nanotube provides anionic electrons in free space inside the tube, which form occupied s-, p-, and d-like superatom states. The outer carbon nanotube layer provides an effective protection for these free-space superatom states from the ambient environment. Such protected superatom states with flexible occupation statuses are expected to have a great potential in various application fields including catalysis and electronics.

INTRODUCTION

Atoms are the fundamental construction unit of materials. The macroscopic properties of materials are thus dictated by the type of bonding presented between the constituting atomic species. However, sometimes, it is more convenient to understand the system properties by considering a number of atoms as a whole. When they can mimic the chemistry of an atom, such groups of atoms are called superatoms. The superatom concept has been widely used to explain the building block character of atomic clusters. When an extended concept, such as super valence bonds, is applied, the stability of even more complicated structure can be understood.

The superatom concept can also be applied to hollow structures where molecular orbitals with atomic characters can be observed. Two recent examples are fullerene C$_{60}$ and carbon nanotubes (CNTs). The electronic structure analysis showed that their superatom states are distinct from those ordinary clusters and come from many-body screening and the corresponding image potentials. These states are called nearly free-electron (NFE) states in layer materials such as graphene. The NFE-like superatom states are mainly distributed in free space (FS) and typically have high energies in the unoccupied conduction band manifold.

When using atoms to build molecules and materials, both occupied and unoccupied atomic orbitals play an important role. Similarly, when using superatom states to understand and tune the properties of the associating system, it is desirable to have both occupied and unoccupied superatom states. For example, nucleophilic and electrophilic active sites may be determined by superatom states with different occupation status. To obtain occupied FS superatom states or lower the energy of superatom states, chemical modifications or external electric fields can be applied, which significantly complicate the superatom concept and restrict its applications. It is thus very desirable to obtain intrinsically occupied FS superatom states.

Because FS superatom states are closely related with NFE states, it is natural to check the availability of occupied partially occupied NFE states in two-dimensional (2D) systems, that is, 2D electron gas in FS (2DEG-FS). Motivated by electrode materials, where electrons distributed in FS act as anions, we have recently designed a Ca$_2$N sheet with 2DEG-FS states. Ca$_2$N monolayer has already been synthesized in the experiment, and the associated 2DEG-FS states are expected to provide an ideal electron-transport channel with minimum scattering from the atomic lattice. We expect that rolling Ca$_2$N monolayer into nanotubes can produce occupied FS superatomic orbitals projected onto the cross section. These states should be chemically very active. To stabilize them, a proper encapsulation protocol should be introduced.

In this study, we systematically investigate the properties of a CNT and Ca$_2$N nanotube composite system (Ca$_2$N@CNT) from first principles. On the basis of energetics from density functional theory (DFT), the stability of the composite system is analyzed. Then, occupied FS superatom states in Ca$_2$N@CNT are predicted from DFT calculations. Finally, we demonstrate that CNT encapsulation can protect these states from attacking of ambient molecules, which is distinct from the Ca$_2$N monolayer case where thicker graphene is required to
provide an effective protection. We expect that realization of such intrinsically occupied FS superatom states will open a new avenue for material design in various fields including catalysis and electronics.

**RESULTS AND DISCUSSION**

As shown in Figure 1, the Ca$_2$N monolayer is compositied of a nitrogen layer sandwiched between two layers of calcium atoms. The unit cell of a Ca$_2$N monolayer contains two calcium atoms in coordination with one nitrogen atom. The optimized lattice parameters are $a = b = 3.60 \, \text{Å}$. The electronic band structure of a Ca$_2$N monolayer is characterized by the partially occupied 2DEG-FS state (see in Figure S1). The Ca$_2$N monolayer has been successfully obtained in a recent experiment.$^{24}$ Ca$_2$N nanotubes are expected to be obtained by the rolling Ca$_2$N monolayer, as demonstrated by the experimental synthesis of CdCl$_2$ nanotubes with a similar structure.$^{25}$

Adopting the nomenclature of CNTs,$^{26}$ we can classify single-wall Ca$_2$N nanotubes by the chiral vector along which the Ca$_2$N monolayer is rolled into a cylindrical nanotube. The chiral vector $\mathbf{C}_h$ can be expressed as a combination of the two basic lattice vectors

$$\mathbf{C}_h = n \mathbf{a}_1 + m \mathbf{a}_2$$

Any Ca$_2$N nanotube can be defined by the two coefficients $(n, m)$. For armchair (Figure 1b) and zigzag (Figure 1c) nanotubes, we have $n = m = 0$, respectively.

The optimized structure of (8, 8) and (14, 0) Ca$_2$N nanotubes is shown in Figure 1b,c. Generally, no significant structure relaxation has been observed, except the strain because of the rolling of the Ca$_2$N monolayer. No strain is detected along the tube direction. For example, the lattice parameter optimized for the zigzag Ca$_2$N nanotube is 6.22 Å, which matches well with $\sqrt{3} \times a_1$ with $a_1$ as the lattice parameter of the Ca$_2$N monolayer.$^{23}$ The strain energy as a function of Ca$_2$N nanotube diameter is shown in Figure 1d. As expected, the strain energy decreases with the nanotube diameter, and it will converge to zero when the diameter becomes infinitely large and the nanotube becomes a monolayer. More importantly, the strain energy of Ca$_2$N nanotubes is smaller than that of MoS$_2$ nanotubes with a similar diameter as shown in Figure S3, which indicates the stability of Ca$_2$N nanotubes.

The ground-state electronic band structure for Ca$_2$N can be well understood from that of the Ca$_2$N monolayer by considering the discretization of the $k$ points enforced by the von Karmann boundary condition along the chiral vector direction.$^{26}$ As a result, similar one-dimensional electron gases in FS (1DEG-FS) states are found in Ca$_2$N nanotubes (Figures 2 and 3). Electron localization function (ELF) analysis clearly shows electron localization on both the interior and exterior

![Figure 1. (a) Chiral vector for armchair and zigzag Ca$_2$N nanotubes. Optimized structure of (b) (8, 8) armchair and (c) (14, 0) zigzag Ca$_2$N nanotubes. (d) Strain energy of Ca$_2$N nanotubes as a function of diameter.](image)

![Figure 2. (a) Band structure of the (8, 8) Ca$_2$N nanotube with (b) ELF map and partial charge densities for seven occupied superatom states. Isosurface value = $3 \times 10^{-4}$ e bohr$^{-3}$. The inset shows the location of occupied superatom-like states.](image)
Ca$_2$N nanotubes are mechanically stable, they require a composite system, we use a composite system with a Ca$_2$N nanotube encapsulated in a CNT. We name it (6, 6)@(17, 17). Bands for s-, p-, and d-superatom-like states in FS are plotted with dashed lines. The inlet shows the location of occupied superatom-like states.

Figure 3. (a) Band structure of the (14, 0) Ca$_2$N nanotube with (b) ELF map and partial charge densities for seven occupied superatom states. Isosurface value = $2 \times 10^{-4}$ e bohr$^{-3}$. The inset shows the radial distribution of the superatom states. The lowest (I < 3) lying NFE states. Such a potential depends on the radius of the nanotube (Figure S4), the superatom states in (6, 6)@(17, 17) are more close to the Fermi level because of charge transfer from many-body screen plays a critical role. The curvature-induced dipole moment change of tubules results in enhanced attractive image potential at the cylindrical center. This enhanced image potential in turn provides stability to low-lying NFE states. Such a potential depends on the radius of the nanotube and is independent of chirality and electronic nature of the tube. In Figure 5, we plot the angle-averaged radial effective potential calculated from DFT and the corresponding radial distribution of the superatom states. The lowest occupied superatom states (I < 3) are stabilized well inside the Ca$_2$N nanotube wall.

Figure 4. (a) Cross section and side view of the (6, 6)@(17, 17) composite system. (b) Ground-state band structure of (6, 6)@(17, 17). Bands from Ca$_2$N nanotubes and CNT are marked in red and black, respectively. Bands for s, p, and d-superatom-like states in FS are plotted with dashed lines.
The band structure of O$_2$-adsorbed (6, 6)@(17, 17) does not show any significant change for superatom states (Figure 6a). At the same time, Bader’s charge population analysis suggests that O$_2$ adsorption does not change the charge population of the inner Ca$_2$N nanotube (24.52 electrons) and that partial charge density for states 1.5 eV below the Fermi level (Figure 6b) also indicates that the superatom states will not be affected by O$_2$ adsorption. This is also confirmed explicitly by the plot of Γ-point charge densities for p ($l=1$) superatom states with the O$_2$-adsorbed (6, 6)@(17, 17) supercell (Figure S8). The superatom states in the CNT-covered Ca$_2$N nanotube are also expected to be less sensitive to the external transverse electric field because of the screening effect of CNT.

## CONCLUSIONS

In summary, we have designed a new 1D composite material with an inner Ca$_2$N nanotube and an outer CNT. In such a system, occupied superatom states in the inner space of the Ca$_2$N nanotube can stably exist in the ambient environment, thanks to the CNT encapsulation. Because they are distributed in the inner space of the Ca$_2$N nanotube, CNT can provide an effective protection to the superatom states. This is different from the case for 2DEG-FS state protection in the Ca$_2$N monolayer, where thicker graphane instead of graphene is required. The results presented here open a new avenue for tuning the chemical activity in a confined low-dimensional space.

## COMPUTATIONAL DETAILS

First-principles calculations were carried out within the framework of DFT using the Vienna ab initio simulation package (VASP).30,31 The projector-augmented wave32,33 method was employed to describe the electron–ion interaction, whereas the exchange–correlation potentials were modeled using the generalized gradient approximation parameterization proposed by Perdew et al. (GGA-PBE).34 In all calculations, the plane wave cutoff energy was set to 500 eV. Structures were fully relaxed until energy and residual forces were converged to values less than 10$^{-5}$ eV and 0.01 eV Å$^{-1}$, respectively. Charge population analysis was carried out by Bader’s atom in molecule method based on electron density topology.35

The nanotube axis was set along the z-axis, and a vacuum region >15 Å was introduced in the x and y directions to eliminate the effects originated from the interactions between two neighboring nanotubes under the periodic boundary condition. A total of 1×1×9 and 1×1×7 k-meshes were used for the calculation of armchair and zigzag Ca$_2$N nanotubes, respectively. The k-mesh used for geometry optimization and static calculations for the (6, 6)@(17, 17) composite system were chosen to be 1×1×5 and 1×1×8,

---

**Table 1. Adsorption Energy ($E_{ad}$) and Charge Transfer ($q_t$) for N$_2$, O$_2$, and H$_2$O Adsorptions at (6, 6)@(17, 17)**

|         | N$_2$  | O$_2$  | H$_2$O |
|---------|--------|--------|--------|
| $E_{ad}$ (eV) | -0.139 | -0.331 | -0.268 |
| $q_t$ (e) | 0.002  | 0.344  | 0.002  |

$^*$Negative sign in $q_t$ corresponds to electron transfer from the adsorbate to the substrate.
respectively. To determine their relative stabilities, we calculated the strain energy of various Ca$_2$N nanotubes in electronvolt per angstrom, which was defined as the energy increase because of the rolling-up of the monolayer

$$E_{\text{strain}} = \left( E_{\text{NT}} - nE_{\text{ML}} \right)/L$$

(2)

where $E_{\text{NT}}$ is the total energy of the nanotube unit cell, $E_{\text{ML}}$ is the energy of the unit cell of the Ca$_2$N monolayer, $n$ is the number of Ca$_2$N units in one nanotube unit cell, and $L$ is the length of the cell along the $z$-axis. When molecular adsorption was considered, an adsorption energy is defined as

$$E_{\text{ad}} = E_{\text{total}} - (E_{\text{substrate}} + E_{\text{molecule}})$$

(3)

where $E_{\text{total}}$ is the energy of the molecular adsorbed system and $E_{\text{substrate}}$ and $E_{\text{molecule}}$ are the energies of the substrate and the molecule, respectively. The more negative the adsorption energy, the stronger is the adsorption.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01575.

Atomic structures of optimized geometries, electronic structures, charge densities, ELF map, and adsorption energies (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: zylj@ustc.edu.cn (Z.L.).

ORCID

Ghulam Abbasi: 0000-0002-4526-4144
Zhenyu Li: 0000-0003-2112-9834
Jinlong Yang: 0000-0002-5651-5340

Author Contributions

G.A and S.Z contributed equally to this work.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was partially supported by the NSFC (21573201), the MOST (2016YFA0200604), the CUSF, and USTC-SCC, SCCAS, Tianjin, and Shanghai Supercomputer Centers.

**REFERENCES**

(1) Khanna, S. N.; Jena, P. Assembling crystals from clusters. *Phys. Rev. Lett.* 1992, 69, 1664–1667.

(2) Castleman, A. W., Jr; Khanna, S. N. Clusters, superatoms, and building blocks of new materials. *J. Phys. Chem. C* 2009, 113, 2664–2675.

(3) Jena, P. Beyond the periodic table of elements: the role of superatoms. *J. Phys. Chem. Lett.* 2013, 4, 1432–1442.

(4) M. R.; Craft, J.; et al. Small-bandgap endohedral metallofullerenes in superatoms. *Angew. Chem., Int. Ed. 2013*

(5) Hoover, S. J.; Petek, H.; et al. A unified view of ligand-protected gold clusters as superatom complexes. *Proc. Natl. Acad. Sci. U.S.A.* 2008, 105, 9157–9162.

(6) Cheng, L.; Yang, J. Communication: New insight into electronic shells of metal clusters: Analogues of simple molecules. *J. Chem. Phys. 2013*, 138, 141101.

(7) Liu, L.; Yuan, J.; Cheng, L.; Yang, J. New insights into the stability and structural evolution of some gold nanoclusters. *Nanoscale 2017*, 9, 856–861.

(8) Cheng, L.; Yuan, Y.; Zhang, X.; Yang, J. Superatom Networks in Thiolate-Protected Gold Nanoparticles. *Angew. Chem., Int. Ed. 2013*, 52, 9035–9039.

(9) Feng, M.; Zhao, J.; Petek, H. Atomlike, hollow-core bound molecular orbitals of C$_{60}$. *Science* 2008, 320, 359–362.

(10) Hu, S.; Zhao, J.; Jin, Y.; Yang, J.; Petek, H.; Hou, J. G. Nearly free electron superatom states of carbon and boron nitride nanotubes. *Nano Lett.* 2010, 10, 4830–4838.

(11) Feng, M.; Zhao, J.; Huang, T.; Zhu, X.; Petek, H. The electronic properties of superatom states of hollow molecules. *Acc. Chem. Res.* 2011, 44, 360–368.

(12) Voora, V. K.; Jordan, K. D. Nonvalence correlation-bound anion states of spherical fullerenes. *Nano Lett.* 2014, 14, 4662–4666.

(13) Posternak, M.; Baldereschi, A.; Freeman, A. J.; Wimmer, E.; Weinert, M. Prediction of electronic interlayer states in graphite and reinterpretation of alkali bands in graphite intercalation compounds. *Phys. Rev. Lett.* 1983, 50, 761–764.

(14) Okada, S.; Oshiyama, A.; Saito, S. Nearly free electron states in carbon nanotube bundles. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2000, 62, 7634–7638.

(15) Silkin, V. M.; Zhao, J.; Guinea, F.; Chulkov, E. V.; Echenique, P. M.; Petek, H. Image potential states in graphene. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2009, 80, No. 121408(R).

(16) Zhao, J.; Petek, H. Non-nuclear electron transport channels in hollow molecules. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2014, 90, 075412.

(17) Liu, Q.-h.; Li, Z.-y.; Yang, J.-l. Nearly free electron state in graphane nanoribbon superlattice. *Chem. Chin. J.* 2011, 24, 22–24.

(18) Cuong, N. T.; Otani, M.; Okada, S. Gate-induced electron-state tuning of MoS$_2$: first-principles calculations. *J. Phys.: Condens. Matter 2014*, 26, 135001.

(19) Khazaei, M.; Ranjarb, A.; Ghorbani-Asl, M.; Arai, M.; Sasaki, T.; Liang, Y.; Yunoki, S. Nearly free electron states in MXenes. *Phys. Rev. B* 2016, 93, 205125.

(20) Zhao, J.; Zheng, Q.; Petek, H.; Yang, J. Nonnuclear Nearly Free Electron Conduction Channels Induced by Doping Charge in Nanotube–Molecular Sheet Composites. *J. Phys. Chem. A* 2014, 118, 7255–7260.

(21) Matsuishi, S.; Toda, Y.; Miyakawa, M.; Hayashi, K.; Kamiya, T.; Hirano, M.; Tanaka, I.; et al. High-density electron anions in a nanoporous single crystal:[Ca$_2$Al$_3$O$_{11}$]$^{4+}$(4e`). *Science* 2003, 301, 626–629.

(22) Lee, K.; Kim, S. W.; Toda, Y.; Matsuishi, S.; Hosono, H. Dicalcium nitride as a two-dimensional electron gas with an anionic electron layer. *Nature 2013*, 494, 336–340.

(23) Zhao, S.; Li, Z.; Yang, J. Obtaining two-dimensional electron gas in free space without resorting to electron doping: an electrode based design. *J. Am. Chem. Soc.* 2014, 136, 13223–13318.

(24) Druffel, D. L.; Kuntz, K. L.; Woomer, A. H.; Alcorn, F. M.; Hu, J.; Donley, C. L.; Warren, S. C. Experimental Demonstration of an Electride as a 2D Material. *J. Am. Chem. Soc.* 2016, 138, 16089–16094.

(25) Zeng, J.; Liu, C.; Huang, J.; Wang, X.; Zhang, S.; Li, G.; Hou, J. UV-light induced fabrication of CdCl$_2$ nanotubes through CdSe/Te nanocrystals based on dimension and configuration control. *Nano Lett.* 2008, 8, 1318–1322.

(26) Hamada, N.; Sawada, S.-i.; Oshiyama, A. New one-dimensional conductors: graphitic microtubules. *Phys. Rev. Lett.* 1992, 68, 1579–1581.

(27) Li, Z.; Yang, J.; Hou, J. G.; Zhu, Q. Is mayenite without clathrated oxygen an inorganic ionicate? *Angew. Chem., Int. Ed.* 2004, 43, 6479–6482.

(28) Gregory, D. H.; Bowman, A.; Baker, C. F.; Weston, D. P. Dicalcium nitride, Ca$_2$N a 2D “excess electron” compound; synthetic routes and crystal chemistry. *J. Mater. Chem.* 2000, 10, 1635–1641.
(29) Pan, X.; Bao, X. The effects of confinement inside carbon nanotubes on catalysis. Acc. Chem. Res. 2011, 44, 553–562.
(30) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 1996, 6, 15–50.
(31) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54, 11169–11186.
(32) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 1758–1775.
(33) Blöchl, P. E.; Jepsen, O.; Andersen, O. K. Improved tetrahedron method for Brillouin-zone integrations. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 49, 16223–16233.
(34) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
(35) Sanville, E.; Kenny, S. D.; Smith, R.; Henkelman, G. Improved grid-based algorithm for Bader charge allocation. J. Comput. Chem. 2007, 28, 899–908.