The operation of lithium-ion batteries involves electron removal from and filling into the redox orbitals of cathode materials, experimentally probing the orbital electron population thus is highly desirable to resolve the redox processes and charge compensation mechanism. Here, we combine quantitative convergent-beam electron diffraction with high-energy synchrotron powder X-ray diffraction to quantify the orbital populations of Co and O in the archetypal cathode material LiCoO$_2$. The results indicate that removing Li ions from LiCoO$_2$ decreases Co $t_{2g}$ orbital population, and the intensified covalency of Co–O bond upon delithiation enables charge transfer from O 2p orbital to Co $e_g$ orbital, leading to increased Co $e_g$ orbital population and oxygen oxidation. Theoretical calculations verify these experimental findings, which not only provide an intuitive picture of the redox reaction process in real space, but also offer a guidance for designing high-capacity electrodes by mediating the covalency of the TM–O interactions.

The orbital population of valence electrons is an important determinant of the physical and chemical properties of functional materials because a large variety of functional properties is controlled by the delicate sensitivity of charge transfer and the orbital electron occupations$^{1,2}$. In recent years, probing and manipulating the orbital configurations in transition-metal oxides have been the backbone of intensive research into physical and chemical fields, such as energy storage and conversion$^1$, electronic devices$^4$, and catalysis$^1$. Among these, the ever-increasing energy consumption in modern society has awakened the strong demand for energy storage devices with higher energy density, durability, and safety$^5$. Lithium-ion batteries (LIBs) have transformed portable electronic devices and become the preferred technology to enable the electrification of road transport due to their outstanding performances in comparison with other rechargeable batteries$^3$. Despite the fact that great progress has been made in terms of cathodes, anodes, and...
electrolytes, the capacity of oxide cathode materials is still the primary bottleneck limiting performances of LIBs\textquotesingle s. As such, much attention has been directed toward revealing the fundamental redox mechanism underlying delithiation and lithiation of cathode materials during battery operation so that novel insights can be obtained to guide the optimization and design of cathode materials. In the classic paradigm, it is tacitly assumed that the electrochemical (de)lithiation of conventional oxide cathode materials is accompanied by the extraction/insertion of electrons from/into the d-orbitals of the transition-metal (TM) ions, indicating that cationic redox chemistry dominates the electrochemical processes of cathode materials. While it has recently become increasingly clear that the lattice oxygen besides TM ions can also participate in the charge compensation in classical layered oxide cathode materials including LiCoO$_2$\textsuperscript{14,15} and LiNi$_{0.33}$Co$_{0.33}$Mn$_{0.33}$O$_2$\textsuperscript{14,15}, especially at high charging cut-off voltage to extract more lithium ions. The intriguing oxygen redox has been attributed to the enhanced LMCT in cathode materials using diffraction techniques\textsuperscript{22–23}. And new knowledge obtained about the orbital populations and electron density redistributions of Co and O atoms enables us to explicitly depict the redox reaction process during delithiation of LiCoO$_2$.

**Results**

**Structure characterization**

It is well known that LiCoO$_2$ cathode adopts the layered α-NaFeO$_2$-type structure with R3m space group and undergoes successive phase transitions from H1 phase to H2, M1, H3, H3', O1 phase during lithium extraction\textsuperscript{2}. In order to facilitate accurate measurement of electron density, we delicately controlled the electrochemical delithiation of single-crystalline LiCoO$_2$ to get single-phase solid solutions with different SOCs at a low rate of 0.1 C (see Supplementary Fig. 1). Atomic-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging demonstrates that as-prepared Li$_{1-x}$CoO$_2$ displays high crystallinity and well-defined layered structure (see Supplementary Fig. 2), which is beneficial for accurate structure factor measurement. The electron density of Li$_{1-x}$CoO$_2$ was determined via multipole modeling of the experimental structure factors with a resolution of $\sin\theta/\lambda \geq 1.2$ Å\textsuperscript{-1} to ensure sufficiently high resolution and precision\textsuperscript{2}. Figure 1 presents a schematic of the entire procedure demonstrating how to map the electron-density distribution in a crystalline material and quantify the orbital population for transition-metal ions under the octahedral crystal field using complementary QCBED and high-energy SPXRD. The crystal structure parameters of Li$_{1-x}$CoO$_2$, including the lattice constants, atomic positions, Debye–Waller factors, and high-order structure factors, can be accurately extracted from SPXRD via Rietveld refinement (see Supplementary Figs. 3–6). To reduce the systematic errors, a low temperature (100 K) was used for all the data collection to minimize the thermal diffuse scattering and anharmonicity that contribute to the background and high-order Bragg reflections, and, finally, to enhance the signal-to-noise ratio of the X-ray diffraction data\textsuperscript{7}. In the meantime, the low-order structure factors were accurately measured via QCBED at 100 K to ensure that the measured X-ray and electron structure factors have nearly the same temperature factors. Besides, we carefully calibrated the beam current for the CBED experiment and evaluated the beam damage, both CBED patterns and electron energy loss spectra showed that the electron dose used in our experiment would not induce the atomic and electronic structures changes at 100 K (Supplementary Figs. 9–10 and Supplementary Tables 1–2). As for the low-order structure factor measurement, the initial structure parameters obtained via Rietveld refinement from SPXRD were employed for the Bloch-wave simulation, in which the thickness, beam direction, and structure factors were treated as refinable parameters. The refinement was made by comparing the experimental intensity profile across CBED systematic rows with the calculated intensity using a goodness-of-fit criterion\textsuperscript{18}. It should be noted that these experimental structure factors are independent of the employed simulation models\textsuperscript{20}. Figure 2 presents the five low-order structure factor measurements for pristine LiCoO$_2$, including (003), (011), (006), (012), and (014), which show good agreement between the experimental and calculated intensities. All of the refined low-order structure factors at different SOCs are listed in supplementary Tables 3–6.

Atom-centered multipole expansion based on the spherical harmonic functions has proven successful in describing the real-space nonspherical electron density\textsuperscript{19}, in which the electron density of each atom is described as follows:

$$\rho(r) = \rho_0 + P_1 r^3 \rho_1(kr) + \sum_{l=0}^{\infty} \sum_{m=-l}^{l} P_{1lm} d_{lm}(\theta, \phi)$$

(1)
where $\rho_c$ and $\rho_v$ denote the core and valence electron densities, respectively; $P_2$ and $P_{\text{lm}}$, the population parameters of the valence electron density and the spherical harmonic density ($d_{\text{lm}}$), respectively; $\kappa$ and $\kappa_\lambda$, valence-shell contraction–expansion parameters; and $R_f$, the radial function. This method implicitly assigns each density fragment to the centered nucleus. Therefore, the shape of the observed electron density can be flexibly fitted by a sum of nonspherical pseudo-atomic densities. These consist of a spherical-atom (or ion) electron density obtained from multiconfiguration Dirac–Fock calculations with variable orbital occupation factors to allow for charge transfer and a small nonspherical part, in which local symmetry-adapted spherical harmonic functions were used.

### Electronic-density distribution and orbital populations

Electronic density and orbital populations in Li$_{1-x}$CoO$_2$

Bader’s quantum theory of atoms in molecules (QTAIM) and deformation densities are often used to analyze the chemical bonding interactions and charge transfer in crystals after obtaining the real-space electron-density distribution. QTAIM can provide a unique logical analysis of the BCPs, as illustrated in Table 1, which indicates that the Co–O interaction is a closed-shell interaction using the bond critical point (BCP), where the electron density is maximum in two directions (perpendicular to the bond) and minimum in one direction (parallel to the bond). To quantify the Co–O bonding interactions of Li$_{1-x}$CoO$_2$ during charging, Bader’s topological analysis was conducted based on the multipole modeling of electron density. The electron-density topological analysis of the BCPs is illustrated in Table 1, which indicates that the Co–O interaction is a closed-shell interaction for the entire charge process, with positive $\nabla^2 \rho(r_c)$ and $|\lambda_l|/|\lambda_s| = 1$. However, the relatively large $\rho(r_c)$ suggests a covalent component in Li$_{1-x}$CoO$_2$, and consequently, the Co–O bond is partially covalent. This may be caused by the high electron density at the positions of the Co nuclei, which results in a sharp decrease along the Co–O bond path and a large curvature ($\lambda_l$) at the BCP.

Deformation density, i.e., the difference between the refined multipole electron density and the reference model constructed from the superposition of the spherical isolated atoms, shows an intuitive charge accumulation and depletion in the chemical bonding regions, as well as deformation around transition metals in line with d-orbital level splitting under the octahedral field. Figure 3 exhibits the static deformation density in the (014) plane, which contains a CoO$_6$ plane of the CoO$_7$ octahedra. In Fig. 3b, the shapes of the Co $e_g$ and $t_{2g}$ orbitals and the O 2p orbital under the octahedral ligand field can be clearly observed. The electron accumulation region surrounding the Co nuclei indicated by red corresponds to the $e_g$ orbital, which has lower energy compared with the $e_g$ orbital (blue region). This deformation density of the pristine LiCoO$_2$ shows that 3d electrons occupy the $e_g$ orbital rather than the $e_g$ orbital of Co atom in the CoO$_6$ octahedra, which agrees with the 3d orbital populations predicted from ligand field model. As can be seen from Fig. 3b–e, it is clear that the accumulation and depletion of the valence electron density in terms of the Co $e_g$ and $e_g$ orbitals become increasingly apparent during lithium extraction, indicating that the difference between the $e_g$ and $e_g$ orbital populations is getting smaller. Meanwhile, the electron density near O atoms also decreased. To verify the experimental results, a supercell consisting of 10 unit-cells with the same c-axis as the primary lattice (see Fig. 4a) was constructed to calculate the total electron-density distribution of Li$_{1-x}$CoO$_2$ using density-functional theory (DFT + U). Figures 4c, e, g present the arrangements of the Li vacancies with the lowest electrostatic energy. To better present the variation of the electron density of both Co and O upon charging, the total electron densities of structures with different Li contents were subtracted from that of pristine LiCoO$_2$. The electron-density difference maps of Li$_{1-x}$CoO$_2$ minus LiCoO$_2$ in Figs. 4d, f, h unambiguously show the electron density within the $e_g$ orbitals and the hole density within the $e_g$ orbitals of Co atoms surrounding the Li vacancies. In addition, a hole density of the $O2p$ orbital pointing towards the Co $e_g$ orbital near the Li vacancies is evident. It is apparent that with an increasing concentration of Li vacancies in the system, more and more electrons are injected into the Co $e_g$ orbital, which is accompanied by an increasing hole density in the Co $e_g$ and $O2p$ orbitals, indicating an LMCT process in Li$_{1-x}$CoO$_2$ induced by Li extraction. Moreover, the difference electron-density maps of Li$_{0.6}$CoO$_2$ minus LiCoO$_2$, Li$_{0.4}$CoO$_2$ minus Li$_{0.6}$CoO$_2$, and Li$_{0.2}$CoO$_2$ minus Li$_{0.4}$CoO$_2$ are illustrated in Figs. 4i–k agrees with the results in Table 2. The agreement between the theoretical calculations...
and the experimental measurements suggests that the combination of QCBED and SPXRD can accurately resolve the electron-density distribution and orbital occupations in crystalline solids.

In addition to the deformation densities, the populations of Co $t_{2g}$ and $e_g$ orbitals under different SOCs were calculated from the refined multipole parameters (Supplementary Table 7). The results can be made more explicit via the orbital occupation numbers as the 3d-orbital electrons can be described in terms of atomic orbitals34, 

$$\rho_{3d} = \sum_{i=1}^{5} P_i d_i^2 + \sum_{i=1}^{5} \sum_{j=1}^{5} P_{ij} d_i d_j$$  \hspace{1cm} \text{(2)}$$

where $d_i = R(r) y_{lm+n}$, $R(r)$ is the radial function; $y_{lm+n}$, the spherical harmonic function; and $P_i$ the population parameter of the atomic orbital. This expression is equal to the valence part of Eq. (1). Therefore, the relationship between the d-orbital occupancies and the multipole population parameters can be expressed in the form of a $15 \times 15$ matrix, which can be further reduced to a smaller size under different site symmetries35. In LiCoO$_2$, the site symmetry of Co is 3m with a $4 \times 4$ matrix, which converts the multipole populations to the $e_g$ and $t_{2g}$ orbital occupancies35, as presented in Table 2. Unlike the principle in ligand field theory that the higher energy $e_g$ orbital should have a zero population for Co in a fully ionic bond, the Co $e_g$ orbital has 1.67 electrons and the O valence shell is not fully filled for pristine LiCoO$_2$. This can be ascribed to the hybridization of the Co $e_g$ orbital and the O 2p orbital as indicated by the covalent component of the Co–O bond37–39. Upon charging process of LiCoO$_2$, on one hand, removing Li ions takes electrons away from Co $t_{2g}$ orbital; on the other hand, oxygen atoms also participate the charge compensation at the high potential in the form of LMCT, leading to the dramatic increased electron populations in Co $e_g$ orbital for Li$_{0.3}$CoO$_2$. This process also induces the decreasing interlayer O–O spacing compared with pristine LiCoO$_2$ as shown in Supplementary Table 8. Moreover, the relationship between the rehybridization and the CoO$_6$ octahedra distortion is evident. Since the bond angle of O–Co–O in the pristine LiCoO$_2$ plane is 85.89° in the pristine LiCoO$_2$ (Supplementary Table 8), it deviates from that (90°) of regular octahedra. And the anisotropic variation of the lattice parameters caused by delithiation further aggravates the distortion of the CoO$_6$ octahedra. As a result, the shorter bond length of the Co–O bond is also beneficial for the rehybridization of the O 2p and Co $e_g$ orbitals (Table 2 and Supplementary Table 8). The lattice distortion and increased oxygen hole density will impair the stability of the lattice structure during delithiation, leading to undesired capacity fading at high voltages. In order to further verify experimental measurements, we performed DFT+U calculations. The variation trend of the electron density distribution and the valence electron orbital populations of Co and O from experimental measurements and theoretical calculations is in accordance with each other, but there still exists deviation in the exact orbital electron populations (Table 2 and Supplementary Table 9). This probably stems from the different partitioning of

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**Fig. 2 | Extraction of the structure factors of pristine LiCoO$_2$.** a Measurements of the low-order structure factors from the energy-filtered CBED (003), (006), (011), (012), and (014) systematic rows. The first row on the left side shows the experimental CBED patterns. The second row presents the corresponding calculated patterns based on the Bloch-wave method. The intensity profiles were extracted from the experimental (dark cyan circles) and refinement results. b Measurements of the high-order structure factors via Rietveld refinement of the SPXRD pattern. The inset shows a magnified region ranging from 32° to 60°.
 electron density between multipole refinement and DFT calculations, and experimentally captured LMCT. For this reason, we performed multipole refinement of LiCoO₂ using the calculated structure factors from WIEN2K and the results were listed in Supplementary Table 10. It can be seen that the obtained orbital populations display a good agreement with experimental results of pristine LiCoO₂, but they are slightly different from DFT+U calculated ones of LiCoO₂ in Supplementary Table 10, indicating the different space partitioning of electron density between DFT+U calculations and experiments. In addition, oxygen redox reaction at the high potential in the form of electron density between DFT+U calculations. 

**Discussion**

In this work, we demonstrated the effectiveness of combining CBED and SXRD to resolve the redox chemistry of LiₓCoO₂ during electrochemical delithiation, by directly visualizing the redistribution of valence electron density and measuring the orbital populations of Co and O atoms. We quantified the number of electrons transfer between the redox orbitals, and found that the extraction of Li ions does not simply take electrons away from the Co eg orbital and in fact, it is accompanied by an electron gain in the Co eg orbital and an increasing hole density in O 2p orbital via rehybridization. Besides, we also successfully detected obvious LMCT at high potential, i.e., in Li₁₋ₓCoO₂, which originated from the increased covalence of Co–O interactions during delithiation. Based on the above findings, it can be concluded that the TM–O interaction determines the charge compensation progress during electrochemical cycling and thus influences the properties and performance of electrode materials. By changing the local chemical environment or the symmetry of the TM–O polyhedron, including doping and elemental substitutions, the interactions between the bonded atoms can be regulated to optimize the performance of electrode materials. Thus, the ability to experimentally trace the variations of the real-space electron density distribution and the orbital occupancy of cathode materials is highly important to guiding the optimization of battery performances and offering a transformational approach for creating new electrode materials.

**Table 1 | Topological analysis of the bond critical points along the Co–O bond in LiₓCoO₂**

| Parameters | LiCoO₂ | Li₀.₆CoO₂ | Li₀.₄CoO₂ | Li₀.₃CoO₂ |
|------------|--------|----------|----------|----------|
| ρ          | 0.5982 | 0.4732   | 0.6817   | 0.6515   |
| Vₚ/ρ       | 10.49  | 15.79    | 13.43    | 15.43    |
| V₂/ρ       | 4.111×10⁻⁶ | 7.982×10⁻⁶ | 1.250×10⁻⁶ | 2.896×10⁻⁶ |
| A₁/λ₃      | 0.17212 | 0.0602   | 0.2868   | 0.0732   |

ρ, Vₚ, and V₂/ρ denote the electron density, its gradient, and the Laplacian, respectively. The Hess eigenvectors are defined by the diagonalization of the symmetric matrix of the nine second derivatives of ρ, Vₚ, and λ₃ denote the Hess eigenvalues perpendicular and parallel to the bond path at the critical point, respectively.

**Methods**

**Sample preparation**

Single-crystalline LiCoO₂ was bought from Alfa with a purity of 99.5%. The delithiated samples were prepared using the electrochemical method. The high-loading electrodes (loading mass of ~100 mg) were charged to different SOCs in a Swagelok cell with Li metal as the counter electrode (1M LiPF₆ in ethylene, dimethyl carbonate). Subsequently, the charged Swagelok cells were disassembled, and the obtained powder samples were washed three times with dimethyl carbonate before drying. All the processes were performed in an argon-filled glove box.

The transmission electron microscopy (TEM) samples were fabricated using focus ion beam (FIB) milling with a FEI Helios 600i. To prevent surface damage from ion milling, a 40-nm-thick carbon layer was deposited via thermal evaporation. On the top of the particle, a regular Pt protection layer was deposited with standard settings using an electron beam at 5 kV and 86 pA for a 300-nm thickness followed by an ion beam at 30 kV and 80 pA for a 1-μm thickness. The particle was then directly lifted to a TEM grid using a nanomanipulator. The thinning process was first performed using the FIB cleaning cross-section method (30 kV, 0.79 nA, and tilt ±2°) until the lamella thickness reached 600 nm. Further fine milling reduced the lamella thickness to 1 Å⁻³, with positive, negative, and zero contours drawn as solid black, dashed black, and solid olive-green lines, respectively. The 3D renderings of the deformation density maps for the Co₆ octahedra are viewed in the same direction as the top model in panel a. The 3D version in panel c can be observed more clearly in Supplementary Fig. 7. The inclined arrows show the [001] direction, and all of the 3D views use the same color scheme. For clarity, the map was plotted by a homemade program, in which a translucency factor (the alpha component in the ARGB color scheme) is used to remove most of the white background.
100 nm (30 kV and 80 pA), and the final polishing process was repeated by FIB at a low voltage and current (8 kV and 23 pA) until the lamella was ~35–50-nm thick. The final polishing step was carefully conducted to avoid lamella bending. To reduce the surface damage and thickness of the amorphous layer, low-energy focused Ar ion milling was conducted using a Fischione 1040 Nano-Mill system.

**QCBED measurements**

The CBED experiments were conducted using an aberration-corrected JEOL-ARM200CF electron microscope equipped with a Gatan imaging filter and 2048 × 2048-pixel 965 CCD camera. The accelerating voltage was calibrated to be 197.50 kV by fitting the kinetically simulated CBED pattern to the experimental one taken from a Si single crystal. An energy window of 10 eV around the zero-loss peak was selected to exclude inelastically scattered electrons, which were not included in the Bloch-wave calculations. Two convergent semi-angles were chosen to obtain the systematic row patterns due to the different \( d \)-spacings of the sample. A custom-developed software based on Bloch-wave theory was employed to fit experimental CBED patterns to obtain the low-order structure factors.

**SPXRD measurements**

Single-crystalline samples of \( \text{Li}_{1-x}\text{CoO}_2 \) were sealed in a Lindeman glass capillary with an internal diameter of 0.3 mm. Synchrotron powder X-ray profiles were measured at the SPring-8 BL19B2 beamline. A large Debye–Scherrer camera with an imaging plate detector was used for the data collection. The data were collected at 100 K using an N2 gas flow low-temperature device. The wavelength of the incident X-rays was 0.413269 Å according to the calibration with a NIST CeO2 standard sample. All data were collected with a \( \sin \theta / \lambda \max \) value of 1.67 Å\(^{-1}\).

**Scanning transmission electron microscopy (STEM) characterization**

STEM imaging was performed on an aberration-corrected JEOL-ARM200CF operated at 200 kV with a convergent semi-angle of 28 mrad and a collection angle from 90 to 370 mrad for high-angle annular dark-field image acquisition.

Table 2 | Co 3d-orbital populations and the number of valence electrons of oxygen obtained from the multipole parameters

| SOC              | Co \( P_{3d} \) | Co \( t_{2g} \) | Co \( e_g \) | O \( P_{\text{valence}} \) |
|------------------|----------------|----------------|-------------|--------------------------|
| \( \text{LiCoO}_2 \) | 6.50(22)       | 4.83(10)       | 1.67(12)    | 6.75(11)               |
| \( \text{Li}_{0.6}\text{CoO}_2 \) | 6.44(27)       | 4.19(14)       | 2.25(13)    | 6.58(13)               |
| \( \text{Li}_{0.4}\text{CoO}_2 \) | 6.66(33)       | 4.26(12)       | 2.40(45)    | 6.37(16)               |
| \( \text{Li}_{0.3}\text{CoO}_2 \) | 7.24(29)       | 2.81(12)       | 4.43(41)    | 6.03(14)               |
Electron energy loss spectroscopy (EELS)
The EELS spectra were acquired in the TEM mode with similar experimental conditions as CBED. An energy dispersion of 0.25 eV/Å and an exposure time of 0.1 s were used to collect EELS spectra before and after electron beam radiation with a radiation time of 2 s to check the beam damage.

Theoretical calculations
We constructed a $\sqrt{3} \times 2 \times 3 \times 1$ supercell containing 120 atoms to calculate the electronic structure of Li$_4$CoO$_2$. The Li$_{30}$Co$_{30}$O$_{60}$ is for pristine LiCoO$_2$; Li$_{15}$Co$_{20}$O$_{60}$ is for Li$_{0.6}$CoO$_2$; Li$_{12}$Co$_{30}$O$_{60}$ is for Li$_{0.4}$CoO$_2$; Li$_{18}$Co$_{30}$O$_{60}$ is for Li$_{0.3}$CoO$_2$. The Vienna Ab Initio Simulation Package (VASP) based on the DFT was used to calculate the electron density and electronic structures of the above LiCoO$_2$, Li$_{0.6}$CoO$_2$, Li$_{0.4}$CoO$_2$, and Li$_{0.3}$CoO$_2$. The Perdew–Burke–Ernzerhof (PBE) functional within a generalized gradient approximation (GGA) form was adopted to treat the exchange-correlation energy. DFT+$U$ ($U=3.32$ eV) was used to correct the self-interaction error of conventional DFT for correlated d electrons in Li$_4$CoO$_2$. A plane wave representation for the wave function with cut-off energy of 500 eV was applied. Geometric optimizations were performed using conjugate gradient minimization until all forces acting on the ion were less than 0.01 eV/Å per atom. The K-point mesh with a spacing of 0.03 Å was adopted.

WIEN2k using a fully-potential linear augmented plane-wave method was adopted to obtain the structure factors of pristine LiCoO$_2$. A plane wave representation for the wave function with cut-off energy of 500 eV was applied. Geometric optimizations were performed using conjugate gradient minimization until all forces acting on the ion were less than 0.01 eV/Å per atom. The K-point mesh with a spacing of 0.03 Å was adopted. The magnetism moments for LiCoO$_2$, Li$_{0.6}$CoO$_2$, Li$_{0.4}$CoO$_2$, and Li$_{0.3}$CoO$_2$ are optimized to 0, 0.4, 0.6, and 0.7 μB/Co.

Data availability
All data supporting this study and its findings are available within the article, its Supplementary Information. All raw data generated during the current study are available from the corresponding authors upon request.

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Author contributions
L.G. and L.W. planned and supervised the project. T.S. and D.X. designed the study and analyzed the CBED and X-ray diffraction data with L.W., V.P., J.Z., and Y.Z. X.R. prepared and electrochemically tested the samples. F.M., X.L., T.L., and X.L. prepared the transmission electron microscopy samples. Q.Z. and Y.W. conducted the scanning transmission electron microscopy measurements and analyzed data with X.W., D.S., Y.S.H., H.L., Q.Y., Z.Z., C.-W.N., and J.Z. A.G., Z.T., and R.X. performed the density-functional theory calculations. T.S., D.X., F.M., Q.Y., L.W., and L.G. wrote the manuscript with the help of the other authors, and all authors revised the manuscript.

Competing interests
The authors declare no competing interests.

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