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# Core-shell TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> anode materials with *in situ* formed nanoscale Co-based interfaces for enhanced lithium-ion transport

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In this study, TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> microspheres with a core-shell structure are successfully synthesized via a homogeneous precipitation method. The composition, structure, and micro-morphology of the prepared microspheres are systematically characterized. The results confirm that spinel Co<sub>3</sub>O<sub>4</sub> uniformly coats the surface of anatase TiO<sub>2</sub> microspheres, forming a lychee-like morphology with excellent dispersibility. The TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> anode material exhibits significantly improved cycling performance, specific capacity, cycling stability, and rate capability compared to commercial graphite. To further investigate the synergistic interaction between TiO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>, *ex situ* characterization, cyclic voltammetry, electrochemical impedance spectroscopy, and theoretical calculations are conducted. In contrast to the layered distribution observed prior to cycling, Co is redistributed in the form of nanoscale CoO and metallic Co particles dispersed across the TiO<sub>2</sub> after cycling, and form a stable interface. Due to interfacial electron accumulation, Ti and Co adopt a higher oxidation state, leading to stronger electron binding. This phenomenon reduces the electrostatic interaction between lithium ions and the surrounding charge, facilitating lithium-ion intercalation/deintercalation and lowering electrode impedance.

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## 1 Introduction

As intermittent green energy sources, such as wind and solar power, become more widely adopted, alongside the rapid expansion of the electric vehicle industry, the demand for enhanced performance, longevity, and safety in energy storage technologies has risen significantly.<sup>1,2</sup> Lithium-ion batteries (LIBs), the most widely used secondary batteries, have attracted significant attention due to their high energy density, long cycle life, and low self-discharge rate.<sup>3–5</sup> In LIBs, anode materials play a pivotal role in facilitating the intercalation and deintercalation of lithium ions, thereby enabling the charging and discharging processes. The performance of anode materials directly determines key battery metrics, including specific capacity, cycle life, rate capability, and safety.<sup>2,6</sup>

Compared with common carbon-based materials,<sup>7,8</sup> alloy materials,<sup>9,10</sup> and various composite materials,<sup>11,12</sup> polycrystalline TiO<sub>2</sub> exhibits minimal volume changes during the intercalation and deintercalation of lithium ions, resulting in excellent cycling stability.<sup>13</sup> However, its applications are constrained by a wide bandgap, low electrical conductivity, and slow lithium-ion transport kinetics.<sup>14,15</sup> Current efforts to optimize TiO<sub>2</sub> anode materials primarily focus on nanostructuring<sup>16</sup> and composite formation.<sup>17,18</sup> Nanostructured TiO<sub>2</sub> anodes significantly enhance the contact area between the material and the electrolyte, increase lithium-ion transport channels, and provide more lithium-ion storage sites, thereby improving their electrochemical performance.<sup>19–22</sup> Due to high energy density, transition metal oxides, Mn<sub>2</sub>O<sub>3</sub>,<sup>23</sup> Fe<sub>2</sub>O<sub>3</sub>,<sup>11</sup> Fe<sub>3</sub>O<sub>4</sub>,<sup>24</sup> CuO,<sup>25</sup> NiO,<sup>26</sup> and Co<sub>3</sub>O<sub>4</sub>,<sup>27</sup> are potential candidates to form composites with TiO<sub>2</sub>.

Common morphologies of TiO<sub>2</sub>-based composite materials include spherical particles, nanoparticles, nanorods, nanofibers, nanotubes, nanobelts, nanosheets, and three-dimensional (3D) array structures. Each morphology imparts distinct electrochemical advantages to the material: spherical structures are beneficial for enhancing packing density and cycling stability;<sup>28</sup> nanoparticles offer high specific surface area and short ion diffusion paths, making them suitable for high-rate applications;<sup>29</sup> one-dimensional structures such as rods,

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Fig. 1 Schematic diagram of preparation of  $\text{TiO}_2@Co_3O_4$  microspheres.

fibers, and tubes provide continuous electron transport pathways and effectively buffer volume expansion—particularly, hollow tubular structures exhibit excellent structural stability;<sup>30,31</sup> nanobelts and nanosheets offer large surface areas and rapid charge transport capabilities;<sup>32,33</sup> while 3D array structures improve overall electrode conductivity and interfacial stability.<sup>34,35</sup>

$Co_3O_4$  reacts with lithium ions to form lithium cobalt oxides and other compounds, enabling lithium-ion storage and release,<sup>36</sup> and providing high energy density of  $890 \text{ mA h g}^{-1}$ .<sup>37</sup> However, the redox reactions of  $Co_3O_4$  during cycling result in continuous phase transformations, causing significant volumetric effects that reduce its cycling stability and the reversibility of redox reactions.<sup>37</sup> Studies indicate that  $TiO_2$  and  $Co_3O_4$  exhibit synergistic effects, whereby the structural stability and excellent cycling performance of  $TiO_2$ , combined with the high specific capacity of  $Co_3O_4$ , allow the synthesis of composite materials that integrate the advantages of both.<sup>36,38–40</sup> Most studies have focused on the reactions and high specific capacity of  $Co_3O_4$ ; however, the interaction between  $Co_3O_4$  and partially coated composite materials raises questions about its actual contribution to battery performance. The underlying mechanisms of the synergistic effects in such composites remain unclear.

In this study,  $TiO_2$  microspheres were used as precursors, and  $Co_3O_4$  was coated on the surface of  $TiO_2$  microspheres *via* a homogeneous precipitation method. The preparation process

of  $TiO_2@Co_3O_4$  microspheres is illustrated in Fig. 1. The composition, structure, and micro-morphology of both  $TiO_2$  and  $TiO_2@Co_3O_4$  microspheres were characterized, and their charge–discharge performance, cycling stability, and rate performance were evaluated. Furthermore, density functional theory (DFT) calculations and electrochemical performance analyses were conducted to compare the material properties before and after coating, revealing the synergistic mechanisms between  $TiO_2$  and  $Co_3O_4$ . This study provides new insights and methodologies for the design and optimization of lithium-ion battery anode materials.

## 2 Results

### 2.1 Phase and morphology

The uncalcined  $TiO_2$  microspheres and cobalt carbonate-coated  $TiO_2$  microspheres were both amorphous (Fig. 2a and S1). After calcination, diffraction peaks corresponding to anatase  $TiO_2$  (ref. 03-065-5714) and spinel  $Co_3O_4$  (ref. 00-043-1003) appeared in the samples, without obvious other impurities peaks. The lattice constants of anatase-phase  $TiO_2$  are  $a$ ,  $b$  = 3.780 Å,  $c$  = 9.515 Å, while those of spinel  $Co_3O_4$  are  $a$ ,  $b$ ,  $c$  = 8.08 Å. This phase structure was further validated by the Raman spectra of  $TiO_2@Co_3O_4$  microspheres (Fig. 2b). The spectrum revealed characteristic vibrational peaks of anatase  $TiO_2$  at Eg(1) ( $142 \text{ cm}^{-1}$ ), B1g ( $394 \text{ cm}^{-1}$ ), A1g ( $252 \text{ cm}^{-1}$ ), and Eg(2) ( $634 \text{ cm}^{-1}$ ),<sup>41</sup> as well as peaks associated with spinel  $Co_3O_4$  at F2g ( $193 \text{ cm}^{-1}$ ), Eg ( $477 \text{ cm}^{-1}$ ), F2g ( $517 \text{ cm}^{-1}$ ), F2g ( $613 \text{ cm}^{-1}$ ), and A1g ( $684 \text{ cm}^{-1}$ ).<sup>42,43</sup>

Surface morphology observations revealed that the anatase  $TiO_2$  microspheres exhibit excellent monodispersity, smooth surfaces, and small pores. The range of particle size is 500 nm to 800 nm, with an average size of 687.4 nm (Fig. 2c, d, S2 and S4). After 4 h of calcination, some  $TiO_2$  microspheres in the  $TiO_2@Co_3O_4$  sample showed pore closure, with  $Co_3O_4$  uniformly coating the surface of  $TiO_2$  microspheres to form

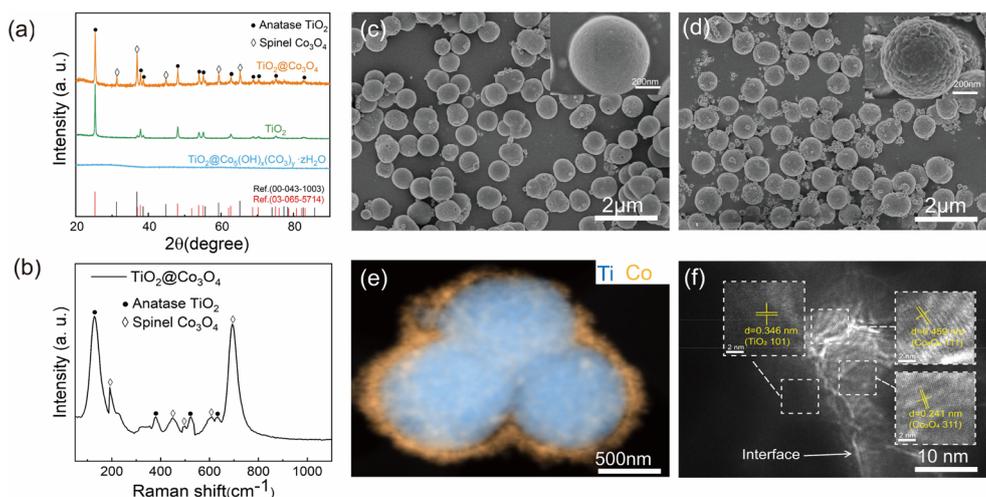


Fig. 2 (a) XRD pattern; (b) Raman spectra of  $TiO_2@Co_3O_4$  microspheres; (c) morphology of  $TiO_2$  after calcination at 600 °C for 4 h; (d) morphology of  $TiO_2@Co_3O_4$  after calcination at 850 °C for 4 h; (e) TEM morphology and elements mapping of calcined  $TiO_2@Co_3O_4$ ; (f) interface between  $TiO_2$  and  $Co_3O_4$  of  $TiO_2@Co_3O_4$  microspheres.



lychee-like microspheres. These microspheres exhibited uniform sizes, regular shapes, good monodispersity, and undamaged surfaces. The surface texture and pore structures facilitate the intercalation and deintercalation of lithium ions. However, when the calcination time was extended to 8 h, the microsphere size increased to approximately 2  $\mu\text{m}$  to 3  $\mu\text{m}$ , with excessive grain growth inside (Fig. S3), resulting in uneven grain size distribution, overfilled interparticle pores, and noticeable aggregation.

To gain deeper insights into the microstructure of the composites, transmission electron microscopy (TEM) was performed, as shown in Fig. 2e and f, together with elemental mapping. The high-resolution transmission electron microscopy (HRTEM) image of the  $\text{TiO}_2@Co_3O_4$  microsphere interface (Fig. 2f) reveals that a uniform  $Co_3O_4$  layer with a thickness of approximately 100 nm is attached to the surface of the  $TiO_2$  microsphere and forms a stable interface with the  $TiO_2$  substrate. This observation indicates that the amorphous  $Co_3O_4$  precursor transformed into a crystalline structure upon calcination, which is consistent with the XRD analysis.

## 2.2 Battery performance analysis

**2.2.1 Charge–discharge tests.** The charge–discharge tests for lithium-ion batteries were conducted at a current density of 0.2 C to prevent accelerated side reactions, such as electrolyte decomposition or lithium metal deposition, under high-rate conditions. This ensured the accuracy, safety, and standardization of the tests. The first discharge and charge profiles of anatase  $TiO_2$  exhibited distinct plateaus at 1.75 V and 2.0 V, respectively (Fig. 3a). During the initial cycle, the battery

demonstrated an initial discharge-specific capacity of 323.9  $\text{mA h g}^{-1}$  and a charge-specific capacity of 155.6  $\text{mA h g}^{-1}$ , corresponding to an initial coulombic efficiency of 48.0%. These results indicate a significant irreversible capacity loss in the first discharge, where lithium ions intercalated into the material were not fully extracted in the subsequent charge. Under the same testing conditions, the charge–discharge profiles of  $Co_3O_4$  anodes are shown in Fig. S5, where the first discharge and charge curve reveals a prominent plateau at approximately 1.2 V and 2.0 V, and  $Co_3O_4$  delivers a high discharge-specific capacity of approximately 508.9  $\text{mA h g}^{-1}$  and a charge-specific capacity of 765.9  $\text{mA h g}^{-1}$ , resulting in an initial coulombic efficiency of 86.9%. In subsequent cycles, the discharge and charge plateaus gradually shift and become smoother, indicating partial structural reconstruction and increased reversibility.

$TiO_2@Co_3O_4$  anodes (Fig. 3b) exhibited discharge and charge plateaus at 1.75 V and 2.0 V, corresponding to lithium-ion intercalation and deintercalation at octahedral sites in anatase  $TiO_2$ . Additionally, stable plateaus were observed between 1.0 V to 1.5 V. During the initial cycle,  $TiO_2@Co_3O_4$  demonstrated an exceptionally high initial discharge-specific capacity of 713.1  $\text{mA h g}^{-1}$ . The initial charge–discharge specific capacities were 713.1  $\text{mA h g}^{-1}$  and 619.0  $\text{mA h g}^{-1}$ , respectively, with a coulombic efficiency of 86.8%. The reversible capacity, defined as the capacity that can be utilized repeatedly during charge–discharge cycles, was 619.0  $\text{mA h g}^{-1}$ . After 2, 3, 10, and 100 cycles, the reversible capacities of  $TiO_2@Co_3O_4$  were 564.6  $\text{mA h g}^{-1}$ , 555.0  $\text{mA h g}^{-1}$ , 495.0  $\text{mA h g}^{-1}$ , and 482.0  $\text{mA h g}^{-1}$ , respectively. These values significantly exceeded those of anatase  $TiO_2$  anodes, which were

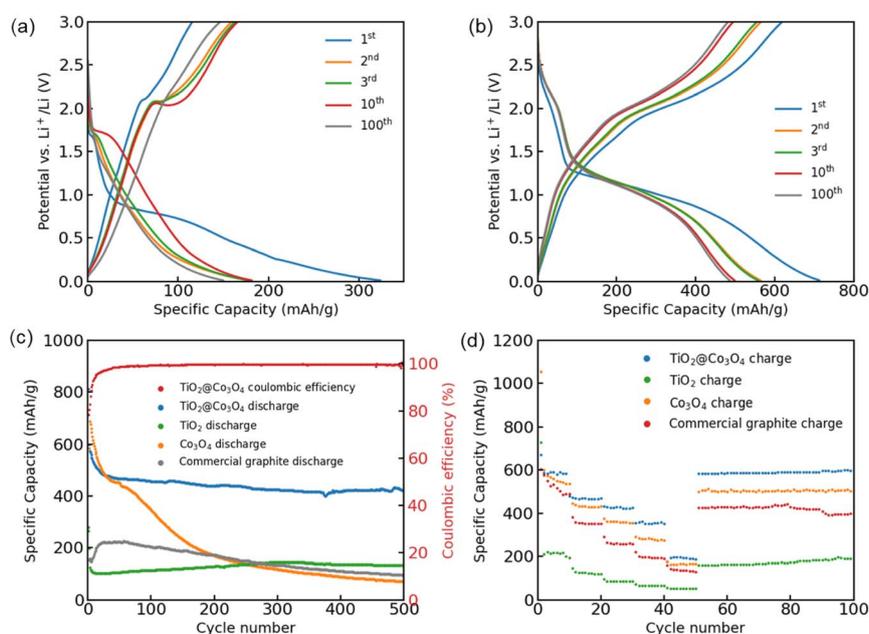


Fig. 3 Charge and discharge curves of anatase  $TiO_2$  (a) and  $TiO_2@Co_3O_4$  (b) for 1, 2, 3, 10, and 100 cycles at a 0.2 C current density; (c) cyclic performance of anatase  $TiO_2$ ,  $TiO_2@Co_3O_4$ , spinel  $Co_3O_4$ , and commercial graphite at a 2 C current density, with the coulombic efficiency diagram of  $TiO_2@Co_3O_4$ ; (d) rate performance of anatase  $TiO_2$ ,  $TiO_2@Co_3O_4$ , spinel  $Co_3O_4$ , and commercial graphite at current densities of 100  $\text{mA g}^{-1}$ , 200  $\text{mA g}^{-1}$ , 400  $\text{mA g}^{-1}$ , 800  $\text{mA g}^{-1}$ , and 1600  $\text{mA g}^{-1}$ .



158.6 mA h g<sup>-1</sup>, 162.7 mA h g<sup>-1</sup>, 165.7 mA h g<sup>-1</sup>, and 146.6 mA h g<sup>-1</sup>, respectively. After 100 cycles, TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> exhibited a capacity improvement of 228.8%. TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> demonstrated extended voltage plateaus, particularly below 1 V, with enhanced charge–discharge stability.

**2.2.2 Cycling performance.** To further evaluate the cycling performance of different materials, half-cells using anatase TiO<sub>2</sub>, spinel Co<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub>, and commercial graphite as anodes were tested at a current density of 2C for 500 cycles. The discharge-specific capacities are shown in Fig. 3c. After 500 cycles, the reversible capacities of anatase TiO<sub>2</sub> and TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> anodes were 132.3 mA h g<sup>-1</sup> and 425.6 mA h g<sup>-1</sup>, respectively, representing a 221.5% improvement for TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub>. This indicates that the coated TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> anode exhibited significantly enhanced capacity even after enduring high current densities and prolonged cycling. Anatase TiO<sub>2</sub> demonstrated a relatively low initial capacity but excellent cycling stability, with minimal capacity degradation, highlighting its inherent stability and suitability for combination with high-capacity materials. In contrast, spinel Co<sub>3</sub>O<sub>4</sub> exhibited a high initial specific capacity (731.3 mA h g<sup>-1</sup>), but its capacity rapidly declined with increasing cycles. After 500 cycles, the reversible capacity of Co<sub>3</sub>O<sub>4</sub> was only 71.4 mA h g<sup>-1</sup>, indicating structural instability during lithium-ion intercalation/deintercalation, leading to volume expansion, material fracture, and deactivation. Commercial graphite exhibited moderate capacity with excellent cycling stability, showing minimal capacity loss over multiple cycles.<sup>43</sup> The capacity of commercial graphite is around 200 mA h g<sup>-1</sup> after 500 cycles, which is relatively high compared to ref. 44. To check the side effects during the cycling, voltage profile of each anode are provided in Fig. S6. For the graphite electrode, the voltage profile still shows the typical plateau below 0.2 V, consistent with the Li<sup>+</sup> intercalation/deintercalation process of commercial graphite, as reported in the literature,<sup>45</sup> indicating no obvious side effects. After 500 cycles, the coulombic efficiency of TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> remained at 99.8%, demonstrating its high reversibility, excellent power output capability, rapid charge–discharge capability, and stable capacity retention. A solid electrolyte interphase (SEI) layer is typically attributed to surface reactions.<sup>13,27</sup> While the initial coulombic efficiency of TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> is only modestly improved compared to TiO<sub>2</sub>, and both values fall within typical ranges for metal oxide anodes. This modest improvement is unlikely to stem solely from changes in the SEI chemistry. More importantly, the TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> electrode shows much better capacity retention and rate capability than both TiO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>, suggesting that the enhancement is sustained during long-term cycling, which cannot be attributed solely to SEI formation in early cycles.

**2.2.3 Rate performance.** Rate performance tests at different charge–discharge rates (Fig. 3d) evaluated the reversible capacities of anatase TiO<sub>2</sub>, TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub>, spinel Co<sub>3</sub>O<sub>4</sub>, and commercial graphite at current densities of 100 mA g<sup>-1</sup>, 200 mA g<sup>-1</sup>, 400 mA g<sup>-1</sup>, 800 mA g<sup>-1</sup> and 1600 mA g<sup>-1</sup>. The reversible capacities were as follows: 217.1 mA h g<sup>-1</sup>, 125 mA h g<sup>-1</sup>, 86.1 mA h g<sup>-1</sup>, 65.6 mA h g<sup>-1</sup> and 52.5 mA h g<sup>-1</sup> for anatase TiO<sub>2</sub>, 559.8 mA h g<sup>-1</sup>, 432.8 mA h g<sup>-1</sup>,

360.7 mA h g<sup>-1</sup>, 283.1 mA h g<sup>-1</sup> and 165.3 mA h g<sup>-1</sup> for spinel Co<sub>3</sub>O<sub>4</sub>, 534.2 mA h g<sup>-1</sup>, 352.1 mA h g<sup>-1</sup>, 259.8 mA h g<sup>-1</sup>, 195.5 mA h g<sup>-1</sup> and 137.6 mA h g<sup>-1</sup> for commercial graphite, and 590.8 mA h g<sup>-1</sup>, 470.1 mA h g<sup>-1</sup>, 429.4 mA h g<sup>-1</sup>, 352.3 mA h g<sup>-1</sup> and 196.1 mA h g<sup>-1</sup> for TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub>. For TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub>, the initial specific capacity at 100 mA g<sup>-1</sup> was approximately 600 mA h g<sup>-1</sup>. As the rate increased, the specific capacity gradually decreased, with a significant drop at 1600 mA g<sup>-1</sup>. However, when the current density returned to 100 mA g<sup>-1</sup>, the capacity recovered to nearly 600 mA h g<sup>-1</sup>, demonstrating excellent rate performance and reversibility. This indicates that high-rate charge–discharge cycles did not significantly compromise the structural integrity of the material.

### 3 Discussion

The enhancement of lithium-ion battery performance by anode materials primarily depends on the intercalation and deintercalation speed of Li<sup>+</sup> and the efficiency of lithium-ion migration within the anode material. During charge and discharge processes, Li<sup>+</sup> ions intercalate into the octahedral sites of anatase-phase TiO<sub>2</sub>, forming a stable phase. The high symmetry of spinel Co<sub>3</sub>O<sub>4</sub>, with a ratio of 1:2 between tetrahedral and octahedral voids, theoretically provides abundant intercalation sites for Li<sup>+</sup>, thereby improving the capacity of TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> batteries.<sup>46</sup> The specific reaction of TiO<sub>2</sub> equations are provided in eqn (1), as well as the multi-step reduction of Co<sub>3</sub>O<sub>4</sub> to Co<sup>0</sup> in eqn (2)–(4).<sup>47</sup>



A noticeable decline in the specific capacity of the TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> electrode is observed during the first 30 charge–discharge cycles, after which the capacity gradually stabilizes beyond 100 cycles. This behavior indicates that irreversible structural transformations occur in the electrode during cycling. To investigate these changes, we disassembled the coin cells after 100 cycles at the end of the charge and discharge states, and performed *ex situ* characterizations.

As shown in Fig. 4a, the *ex situ* XRD patterns of the electrodes after 100 cycles reveal the absence of Co<sub>3</sub>O<sub>4</sub> diffraction peaks. Instead, characteristic peaks corresponding to metallic Co and CoO are detected, which is consistent with the proposed electrochemical conversion reactions. The *ex situ* HRTEM image under the discharged state (Fig. 4b) shows that cobalt is partially present in the form of cobalt monoxide (CoO), with the (111) lattice plane clearly observed, having a *d*-spacing of 0.248 nm. Elemental mapping by EDX indicates that Co is dispersed in dot-like patterns on the TiO<sub>2</sub> matrix surface.



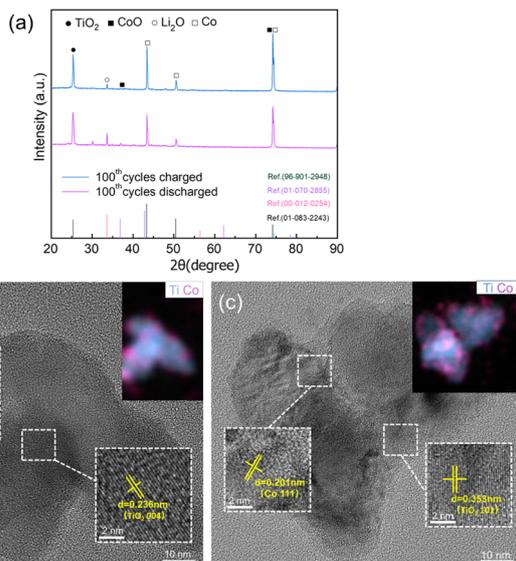


Fig. 4 *Ex situ* testing of active materials of the 100th cycle under 2 C: (a) XRD; (b) discharged HRTEM; (c) charged HRTEM.

In the charged state, the anatase  $\text{TiO}_2$  structure, as evidenced by the (101) plane with an interplanar spacing of 0.353 nm. Meanwhile, Co remains present on the surface in large quantities, and its lattice spacing of 0.201 nm corresponds to the (111) plane of metallic Co. These results suggest that after prolonged cycling, the original nanoscale shell structure of  $\text{Co}_3\text{O}_4$  breaks down. The initially continuous film-like coating transforms into discrete Co and CoO nanoparticles. Additionally, a small amount of  $\text{Li}_2\text{O}$  is present, although its detection is primarily inferred from XRD due to the low atomic weight of lithium. Following this structural transformation, the electrode enters a relatively stable state, as reflected in the stabilization of the specific capacity over continued cycling.

Based on the *ex situ* XRD, 4 heterojunctions were constructed from fully relaxed anatase  $\text{TiO}_2$ ,  $\text{Co}_3\text{O}_4$ , CoO, Co and  $\text{Li}_2\text{O}$  (Fig. S7). The equilibrium lattice parameters of bulk structures are listed in Table S2.

Five-layers films (Fig. S9 and S10) were cleaved from the (101) high-energy plane of anatase  $\text{TiO}_2$  and the (111) high-energy plane of spinel  $\text{Co}_3\text{O}_4$ , CoO, Co and  $\text{Li}_2\text{O}$ .<sup>48,49</sup> These layers are illustrated in Fig. 5a and b, along with the electron localization function (ELF). The lattice parameters of the  $\text{TiO}_2@ \text{Co}_3\text{O}_4$  heterojunction are  $a = 11.280 \text{ \AA}$ ,  $b = 10.280 \text{ \AA}$ , and  $c = 40 \text{ \AA}$ . No significant lattice distortion was observed around the interface. ELF analysis revealed no electron accumulation along the Ti–O and Co–O bonds of  $\text{TiO}_2@ \text{Co}_3\text{O}_4$  and  $\text{TiO}_2@ \text{CoO}$ ; instead, electrons were localized around the ions, indicating the ionic nature of these bonds. Specifically, the electron behavior near the interface was consistent with that in the sub-junctions. The bonding states of Ti–O and Co–O of  $\text{TiO}_2@ \text{Co}_3\text{O}_4$  were confirmed by the positive integrated crystal orbital Hamilton population (ICOHP) values (Fig. S11), suggesting the formation of a stable heterojunction.

To elucidate the charge transfer behavior at the interface, we calculated the charge density difference in the interface models.

The results show charge accumulation at the interface in all four models. To quantitatively evaluate the extent of charge transfer, we compared the Bader charges of atoms near the interface with those in the individual sub-junctions. The average Bader charges of Ti and Co atoms on either side of the  $\text{TiO}_2@ \text{Co}_3\text{O}_4$  interface are found to be 2.29+ and 1.50+, respectively, which are higher than those in the sub-junctions, where the charges are 2.24+ and 1.39+. This indicates an increase in the oxidation states of Ti and Co near the interface. If we separate the heterojunction into two parts by the interface, the amount of charge transferred across the interfaces of  $\text{TiO}_2@ \text{Co}_3\text{O}_4$ ,  $\text{TiO}_2@ \text{CoO}$ ,  $\text{TiO}_2@ \text{Co}$ , and  $\text{TiO}_2@ \text{Li}_2\text{O}$  are 8.90e, 3.04e, 1.82e, and 0.91 e, respectively.  $\text{TiO}_2@ \text{CoO}$  exhibits greater charge transfer than  $\text{TiO}_2@ \text{Co}$ , suggesting faster  $\text{Li}^+$  insertion due to charge accumulation on the CoO side. As the reaction proceeds toward  $\text{TiO}_2@ \text{Co}$ , the insertion becomes slower while delithiation becomes easier, contributing to the observed cycling behavior.

To further confirm the oxidation state variation, the high-resolution X-ray photoelectron spectroscopy (XPS) was conducted on the grown core–shell structures. As shown in Fig. 5e, the Co 2p region of  $\text{Co}_3\text{O}_4$  (Fig. 5f) features four distinct peaks: two prominent main peaks and two satellite peaks. The main peaks correspond to Co 2p<sub>3/2</sub> at 780 eV and Co 2p<sub>1/2</sub> at 795 eV. For the  $\text{TiO}_2@ \text{Co}_3\text{O}_4$  structure, these peaks shift toward higher binding energies, consistent with our theoretical calculations. Fig. 5g and h present the Ti 2p spectra for  $\text{TiO}_2$  and  $\text{TiO}_2@ \text{Co}_3\text{O}_4$ , respectively. In  $\text{TiO}_2$ , three peaks are observed, including two main peaks at 459.0 eV and 464.5 eV, corresponding to Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub>, as well as a satellite peak. After the formation of the composite, a noticeable shift in binding energy suggests an increased oxidation state of Ti, which is in line with the results from Bader charge analysis.

Cyclic voltammetry (CV) tests conducted with half-cells using  $\text{TiO}_2$ ,  $\text{TiO}_2@ \text{Co}_3\text{O}_4$ , and  $\text{Co}_3\text{O}_4$  as anode materials are shown in Fig. 6a and b, and S12. For the  $\text{TiO}_2$  electrode, the first scan exhibited a reduction peak at 1.7 V and an oxidation peak at 2.2 V, corresponding to the initial discharge and charge processes, respectively. These redox peaks are characteristic of the  $\text{Li}^+$  intercalation/deintercalation reactions in anatase  $\text{TiO}_2$ , indicating good reversibility. The specific reaction equation is provided in eqn (2).<sup>50,51</sup> During the first scan, the current response was relatively low, suggesting limited electrochemical activity during the initial scan. However, a slight increase in current response was observed during the second scan, indicating that the electrode surface became more active after the initial cycle or that some degree of structural changes occurred in the material. As the current further increased during the third scan, it suggested that the electrochemical behavior of the electrode material had stabilized after multiple cycles. The subtle differences between the CV curves for different scans highlight the progressive activation of the electrode material. With increasing scan numbers, the current peaks gradually grew, implying that the activation process of the electrode material or changes in surface structure led to an enhanced reaction rate over time.



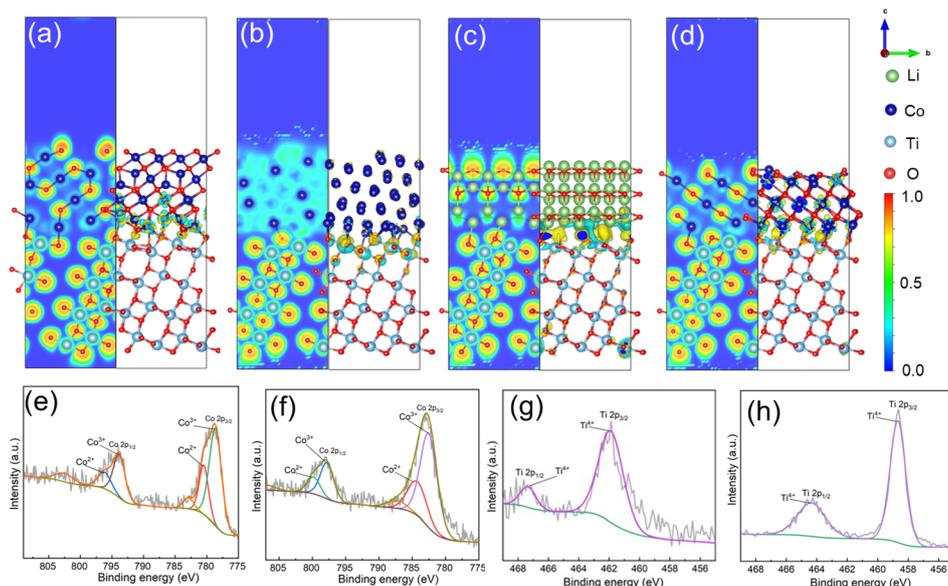


Fig. 5 The heterojunction model of  $\text{TiO}_2@Co_3O_4$  (a),  $\text{TiO}_2@Co$  (b),  $\text{TiO}_2@Li_2O$  (c) and  $\text{TiO}_2@CoO$  (d). The displaying ELF map is illustrated on the left and the charge difference on the right, where the isosurface is set at 0.005 and marked by positive (yellow) and negative (cyan) regions. To provide a details of the selected planes, the 3D figures of ELF figures are shown in Fig. S10. The XPS spectrum of Ti (e and f) and Co (g and h) before (e and g) and after cycling.

The CV curves of the  $\text{TiO}_2@Co_3O_4$  material (Fig. 6b) not only exhibit the redox characteristics of anatase  $\text{TiO}_2$  but also display a reduction peak at 1.0 V during the first scan, corresponding to the multi-step reduction of  $Co_3O_4$  to  $Co^0$ . The specific reaction equations are provided in eqn (3)–(5). Additionally, the

$\text{TiO}_2@Co_3O_4$  material exhibits higher current responses, indicating more intense electrochemical reactions under these experimental conditions. This suggests enhanced lithium-ion conductivity or improved electron transport properties. Notably, during the second and third scans, the current density

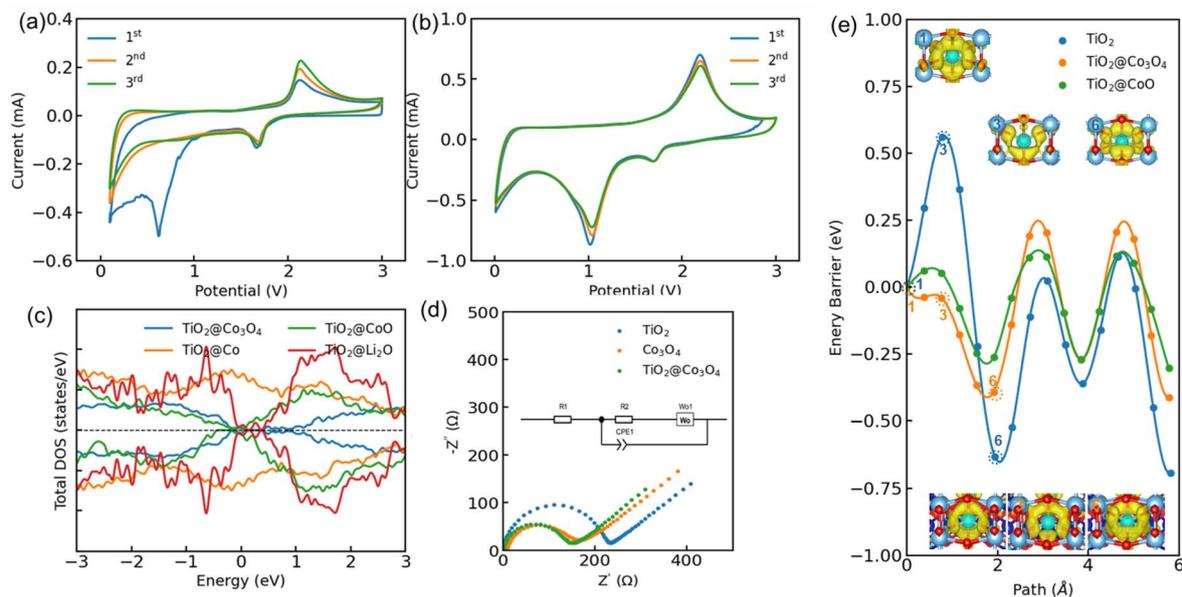


Fig. 6 CV curve of anatase  $\text{TiO}_2$  (a) and  $\text{TiO}_2@Co_3O_4$  (b) with a scanning speed of  $0.3 \text{ mV s}^{-1}$  and a voltage window of 0.01 V to 3.0 V; (c) total DOS of the films; (d) Nyquist plots of  $\text{TiO}_2$ ,  $\text{TiO}_2@Co_3O_4$ , and  $Co_3O_4$  in the frequency range of  $1 \times 10^{-2} \text{ Hz}$  to  $1 \times 10^6 \text{ Hz}$ . The inset shows the equivalent circuit diagram, where CPE1 represents the double-layer capacitance,  $R_1$  represents the internal resistance of the battery,  $R_2$  represents the charge transfer resistance, and  $Wo_1$  represents the Warburg coefficient for lithium-ion diffusion.<sup>54</sup> (e) Calculated lithium-ion migration energy barriers in  $\text{TiO}_2$ ,  $\text{TiO}_2@Co_3O_4$  and  $\text{TiO}_2@CoO$  along the migration path shown in Fig. S13. 6 inset figures illustrates the charge difference at sites 1, 3, and 6. The isosurface level is set to 0.005, with yellow indicating charge accumulation and cyan representing charge depletion.



increases significantly, suggesting progressive activation at the interface and a substantial enhancement in the  $\text{Li}^+$  intercalation/deintercalation rate. The current variations observed over the three scans are relatively similar, indicating that the electrochemical behavior of the electrode material stabilizes after the second scan.

The activation of the anodes can be confirmed by the density of states (DOS) analysis. The calculated bandgap of thin-film  $\text{TiO}_2$  is 2.47 eV (Fig. 6c), which is lower than the experimental value of 3.2 eV.<sup>52</sup> It should be noted that the generalized gradient approximation (GGA) functional cannot accurately describe the d-orbitals of transition metals, leading to an underestimation of bandgap widths. Typically, a Hubbard  $U$  correction is introduced to obtain more accurate bandgap values; however, an excessively high  $U$  value can distort the band structure. In this study, a moderate  $U$  value was adopted. Meanwhile, the calculated bandgap values of spinel  $\text{Co}_3\text{O}_4$  are 1.08 eV, 0.31 eV, and 1.54 eV for bulk, thin film, and experimental measurements, respectively.<sup>53</sup> After forming the composite, the bandgap of  $\text{TiO}_2@Co_3O_4$  decreases compared to that of pure  $\text{TiO}_2$  (Fig. 6c). Compared to  $\text{TiO}_2@Co_3O_4$ , the density of states (DOS) of  $\text{TiO}_2@CoO$  indicates higher electronic conductivity, while  $\text{TiO}_2@Co$  exhibits metallic behavior. This suggests that the electrode material after cycling is expected to possess lower internal resistance.

The electrochemical impedance spectroscopy (EIS) results of anatase  $\text{TiO}_2$ , spinel  $\text{Co}_3\text{O}_4$ , and  $\text{TiO}_2@Co_3O_4$  anodes are shown in Fig. 6d. Based on the lithium-ion intercalation and deintercalation mechanisms in the anodes, the equivalent circuit illustrated in the inset of Fig. 6d was used to fit the EIS spectra. The results show that the internal resistances of anatase  $\text{TiO}_2$ , spinel  $\text{Co}_3\text{O}_4$ , and  $\text{TiO}_2@Co_3O_4$  are 23.81  $\Omega$ , 11.67  $\Omega$ , and 4.95  $\Omega$ , respectively, while the charge transfer resistances are 223.72  $\Omega$ , 186.21  $\Omega$ , and 161.41  $\Omega$ , respectively. The internal resistance of  $\text{TiO}_2@Co_3O_4$  is significantly lower than those of the other two materials, and its conductivity is markedly higher. Under high-rate (rapid charge-discharge) conditions, batteries require rapid charge transfer, and lower charge transfer resistance contributes to maintaining high electrochemical reaction efficiency.

After lithium intercalation, lithium ions migrate inward from the interface along the octahedral interstitial channels of  $\text{TiO}_2$  (Fig. S13), including 16 potential migration states. Lithium ions follow a pathway where electrons traverse the Ti-O bonds *via* a Ti-O-Ti-O conduction route to the next Ti-O bond, forming a continuous conductive path.<sup>54</sup> During migration, charge transfers from lithium ions to the bonding sites, and reducing Co and Ti. Conversely, during delithiation, these transition metals are reoxidized. For  $\text{TiO}_2$  anodes, the initial lithium-ion migration exhibits an energy barrier of approximately 0.61 eV (Fig. 6e), and the barrier increases to around 0.8 eV within the anode. In contrast, the  $\text{TiO}_2@CoO$  presents a energy barrier of 0.28 eV, while the  $\text{TiO}_2@Co_3O_4$  composite shows nearly no energy barrier at the initial migration stage, indicating easier lithium-ion transport through the surface layer. The internal energy barrier of the composite is approximately 0.6 eV, lower than that of  $\text{TiO}_2$  and  $\text{Co}_3\text{O}_4$  (Fig. S14).

Charge differential calculations (Fig. 6e) reveal significant charge fluctuations in the  $\text{TiO}_2$  anode, particularly at sites 1 and 6, where charge shifts toward Ti atoms compared to site 3. In contrast, the  $\text{TiO}_2@Co_3O_4$  composite exhibits more stable charge transfer, indicating lower resistance during lithium-ion migration. Bader charge analysis shows that the charges at sites 1, 3, and 6 in  $\text{TiO}_2@Co_3O_4$  are 0.846+, 0.854+, and 0.863+, respectively, compared to 0.855+, 0.853+, and 0.869+ in  $\text{TiO}_2$ . The higher electron loss at site 1 of  $\text{TiO}_2@Co_3O_4$  suggests stronger charge transfer at this site. Due to the bonding state of Ti-O and Co-O at the composite interface (with ICOHP values of -1.406 and -1.330, respectively), charges transfer from  $\text{TiO}_2$  and  $\text{Co}_3\text{O}_4$  to the interface (Fig. 5a). At this stage, the surface Ti atoms exhibit charges of 2.29+, higher than the 2.24+ observed in  $\text{TiO}_2$ . This indicates that Ti atoms at the interface are in a higher oxidation state, which enhances their binding to surrounding electrons and reduces the binding of lithium ions, facilitating lithium-ion migration and lowering electrode impedance.

## 4 Conclusions

In this study,  $\text{TiO}_2@Co_3O_4$  composite microspheres were successfully synthesized *via* a homogeneous precipitation method.  $\text{Co}_3\text{O}_4$  was uniformly coated on the  $\text{TiO}_2$  surface, forming lychee-shaped microspheres with good dispersibility, where  $\text{Co}_3\text{O}_4$  accounted for 34.99% of the microsphere surface, and focused on understanding the synergistic effects between  $\text{TiO}_2$  and  $\text{Co}_3\text{O}_4$ . XRD and Raman spectroscopy analyses confirmed that the material consists of anatase  $\text{TiO}_2$  and spinel  $\text{Co}_3\text{O}_4$ . After 100 cycles at a current density of 0.2 C, the specific capacity of the composite reached 482  $\text{mA h g}^{-1}$ , representing a 228.8% improvement over the capacity of pure  $\text{TiO}_2$  anodes. After 500 cycles at 2C, the discharge-specific capacity of  $\text{TiO}_2@Co_3O_4$  remained at 385.64  $\text{mA h g}^{-1}$ , with a capacity retention rate of 64.46%.

*Ex situ* characterization of the electrode materials after 100 cycles, where the specific capacity had stabilized, reveals that the active components exist in the form of  $\text{TiO}_2$ , metallic Co, and CoO. In contrast to the layered distribution observed prior to cycling, Co is redistributed in the form of nanoscale CoO and metallic Co particles dispersed across the  $\text{TiO}_2$  matrix after cycling. XPS measurements combined with DFT calculations show that the binding energies of both Ti and Co increase significantly upon formation of the  $\text{TiO}_2@Co_3O_4$  heterostructure. This suggests that interfacial electron accumulation elevates the oxidation states of the transition metals. The higher oxidation states enhance the electrostatic binding of surrounding electrons, thereby reducing the electrostatic drag on lithium-ion migration, improving ionic mobility, and lowering internal resistance.

## 5 Experiment and computational details

### 5.1 Preparation of $\text{TiO}_2$ microsphere precursors

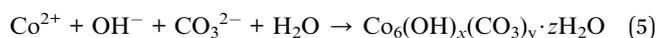
$\text{TiO}_2$  microspheres were synthesized using a modified low-temperature Stöber method.<sup>55</sup> Tetrabutyl titanate (TBOT) was used as the titanium source, and anhydrous ethanol served as



the solvent. A solution of 2 mL 0.01 mol L<sup>-1</sup> KCl in 400 mL anhydrous ethanol was added to a low-temperature reaction tank and stirred for 1 h using a cryogenic circulating pump to reduce the temperature. When the temperature reached -13 °C, 16 mL TBOT was rapidly added and stirred for 5 min to ensure uniform mixing. The mixture was then allowed to stand at low temperature for 4 h. The precipitate was collected *via* centrifugation and alternately washed three times with anhydrous ethanol and deionized water. Finally, the amorphous TiO<sub>2</sub> microspheres were obtained through freeze-drying and calcined at 600 °C for 2 h at a heating rate of 5 °C min<sup>-1</sup> to produce anatase-phase TiO<sub>2</sub>. The details of the reagents used in the preparation process are provided in the supporting materials (Table S1).

## 5.2 Preparation of TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> microspheres

To prepare TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> microspheres, 0.32 g of TiO<sub>2</sub> microspheres, 0.712 g ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>), and 100 mL deionized water were added to Beaker A and ultrasonically dispersed for 30 min. Meanwhile, 0.4758 g cobalt(II) chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O) was dissolved in 100 mL deionized water in Beaker B, followed by the addition of 0.2424 g urea. The solution in Beaker B was stirred with a glass rod until completely dissolved. After ultrasonic dispersion of the solution in Beaker A was completed, the solution from Beaker B was slowly poured into Beaker A under magnetic stirring for 30 min. The mixture was then heated and stirred in a water bath at 60 °C for 10 h. After the reaction, the product was collected *via* centrifugation and washed alternately three times with deionized water and ethanol. The washed product was dried in an oven at 80 °C and then calcined at 850 °C for 4 h to produce TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> microspheres. The thermal decomposition of basic cobalt carbonate<sup>38</sup> follows the reactions:



## 5.3 Structural analysis and characterization

The crystal structure of the samples was analyzed using an X-ray powder diffractometer (XRD, PANalytical, Netherlands) with a Cu target, operating at 40 kV and 40 mA. Raman spectroscopy (XploRA, Horiba) was employed to characterize the structural features of the samples, utilizing a laser with a wavelength of 532 nm and a frequency range of 50 cm<sup>-1</sup> to 1200 cm<sup>-1</sup>. The chemical composition and atomic structure of the samples were examined using an X-ray photoelectron spectrometer (PHI5000 VersaProbe III, ULVAC-PHI). The sample morphology and energy-dispersive X-ray spectroscopy (EDS) measurements were conducted using a scanning electron microscope (SEM, JSM-5800, JEOL, Japan). High-resolution transmission electron microscopy (HRTEM) was performed using a Thermo Scientific Talos F200X microscope operated at an accelerating voltage of

200 kV. X-ray Photoelectron Spectroscopy (XPS) measurements were carried out using a PHI 5000 VersaProbe I spectrometer equipped with a monochromatic Al K $\alpha$  X-ray source.

## 5.4 Electrode preparation and electrochemical performance testing

The active material, Super P carbon black, and polyvinylidene fluoride (PVDF) were weighed in a mass ratio of 7 : 2 : 1 and thoroughly mixed and ground in an agate mortar. The resulting mixture was transferred to a beaker, and an appropriate amount of *N*-methyl-2-pyrrolidone (NMP) was added. The solution was magnetically stirred until a viscous slurry was obtained. The slurry was evenly coated onto copper foil using a blade with a 20  $\mu\text{m}$  gap to form electrode sheets, which were dried at 80 °C for 12 h. Circular electrodes with a diameter of 15 mm were then punched out. A 1 M LiPF<sub>6</sub> solution in a solvent mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (vol% = 1 : 1 : 1) was used as the electrolyte. Polypropylene membranes (Celgard 2500) were used as the separator, and lithium metal served as both the counter electrode and the reference electrode. The CR2032 coin cells were assembled in an argon-filled glovebox. Galvanostatic charge-discharge testing (voltage range: 0.01 V to 3.5 V vs. Li<sup>+</sup>/Li) was conducted using a LAND battery testing system (Land CT2001A). Cyclic voltammetry (CV, scan rate: 0.1 mV s<sup>-1</sup>) and electrochemical impedance spectroscopy (frequency range: 10<sup>-2</sup> Hz to 10<sup>6</sup> Hz) were performed using an electrochemical workstation (CS350M).

## 5.5 DFT simulation

Self-consistent density functional theory (DFT) calculations were carried out using the Vienna *Ab initio* Simulation Package (VASP).<sup>56–58</sup> The revised Perdew–Burke–Ernzerhof functional for solids (PBEsol)<sup>59</sup> within the generalized gradient approximation (GGA) was employed. The plane-wave cutoff energy was set to 450 eV, and the total energy was minimized until the energy difference between successive electronic iterations was less than 10<sup>-6</sup> eV. Structural relaxation continued until all forces were reduced to below 0.1 eV Å<sup>-1</sup>. The GGA + U method was applied<sup>60</sup> with *U* values of 2.5 eV for Ti<sup>61,62</sup> and 3.0 eV for Co.<sup>63,64</sup> The explicitly treated electrons included: 3p<sup>6</sup>4s<sup>2</sup>4d<sup>2</sup> (Ti), 3d<sup>7</sup>4s<sup>2</sup> (Co), 2s<sup>2</sup>2p<sup>4</sup> (O), and 1s<sup>2</sup>2s<sup>1</sup> (Li). The initial magnetic moments were set to 0 for Co<sup>3+</sup> and 3.00  $\mu_B$  for Co<sup>2+</sup>. Crystal Orbital Hamilton Population (COHP) analysis was performed using the Lobster code.<sup>65</sup> The Bader charge analysis was conducted with the Bader code.<sup>66</sup>

## Author contributions

Conceptualization: Yuan Chen, Weiliang Ma; data curation: Hao Li, Weiliang Ma, Li Chen, Yi Yang; formal analysis: Hao Li, Weiliang Ma, Yi Yang; funding acquisition: Yuan Chen, Weiliang Ma; investigation: Yuan Chen, Weiliang Ma; methodology: Yuan Chen, Weiliang Ma, Marie-Christine Record, Pascal Boulet; project administration: Yuan Chen, Weiliang Ma; resources: Weiliang Ma, Yuan Chen, Marie-Christine Record, Pascal



Boulet; software: Weiliang Ma, Marie-Christine Record, Pascal Boulet supervision: Yuan Chen, Weiliang Ma; validation: Hao Li; visualization: Hao Li, Weiliang Ma, Huawei Luo; writing – original draft: Weiliang Ma, Hao Li; writing – review & editing: Yuan Chen, Yi Yang, Jan-Michael Albina, Juan Wang.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

Data for this article, including XRD, Raman spectrum, VASP inputs, Bader charge analysis, charge–discharge performance, cycling performance, rate performance, CV curves and Nyquist curves are available at [[https://github.com/leon-venir/paper\\_data/blob/main/y25\\_li\\_data.zip](https://github.com/leon-venir/paper_data/blob/main/y25_li_data.zip)].

Supplementary information includes additional figures (SEM images, bonding analysis), detailed modelling procedures, and supporting tables of measurement data. See DOI: <https://doi.org/10.1039/d5ra04485e>.

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