

Article

Zeolitic Imidazolate Framework 67-Derived Ce-Doped CoP@N-Doped Carbon Hollow Polyhedron as High-Performance Anodes for Lithium-Ion Batteries

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Abstract: Zeolitic Imidazolate Framework 67 (ZIF-67) and its derivatives have attracted extensive interest for lithium-ion batteries (LIBs). Here, Cerium-doped cobalt phosphide@nitrogen-doped carbon (Ce-doped CoP@NC) with hollow polyhedron structure materials were successfully synthesized via ionic-exchange with Co and Ce ions using the ZIF-67 as a template followed with a facile low-temperature phosphorization treatment. Benefitting from the well-designed hollow polyhedron, steady carbon network, and Ce-doping structural merits, the as-synthesized Ce-doped CoP@NC electrode demonstrated superior performance as the anode in LIBs: a superior cyclability (400 mA h g^{−1} after 500 cycles) and outstanding rate-capability (590 mA h g^{−1}, reverted to 100 mA g^{−1}). These features not only produced more lithium-active sites for LIBs anode and a shorter Li-ion diffusion pathway to expedite the charge transfer, but also the better tolerance against volume variation of CoP during the repeated lithiation/delithiation process and greater electronic conductivity properties. These results provide a methodology for the design of well-organized ZIFs and rare earth element-doped transition metal phosphate with a hollow polyhedron structure.

Keywords: hollow polyhedron; Ce-doped CoP; N-doped carbon; lithium-ion batteries; anode



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1. Introduction

The growing demands on energy storage technology for commercial energy storage markets drive the exploration of LIBs with outstanding rate-capability as well as longer cycling stability [1–5]. At present, extensive efforts have been devoted to developing new-type high-capacity anode materials in LIBs. Transition metal phosphides (TMPs) have been widely investigated as an alternative anode for lithium storage due to their high theoretical capacities, low costs, and the lithiation product of Li₃P from TMPs with higher conductivity (Li₃P: ~1 × 10^{−4} S cm^{−1}) (Li₂O from similar metal oxides: ~5 × 10^{−8} S cm^{−1}; Li₂S from similar metal sulfides: ~1 × 10^{−13}) [6–10]. Among the various TMPs for LIBs, cobalt phosphide (CoP) with a high theoretical capacity (~894 mA h g^{−1}) and relatively low redox potential (~0.6 V) attracts great interests [11–14]. However, the dramatic volume variation of CoP during cycling results in the destruction of the electrode structure and rapid capacity fading. Simultaneously, its intrinsically inferior electrical conductivity usually causes poor rate capability. To address these issues, various improvement measures have been reported to tune the structure at nanoscale-to-microscale and improve the conductivity of CoP [15–20].

ZIF-67 materials have been widely used as precursors to synthesize diverse functional materials via pyrolysis reactions at different temperatures or a series of chemical

reactions with relevant chemical reagents. ZIF-67-derived nitrogen-doped carbon-based carbides, oxides, phosphides, and chalcogenides have the characteristics of high chemical/mechanical stabilities, controllable structures/compositions, and large surface area, utilizing the modification of physical/chemical properties and the improvement of energy storage performance. The construction of hollow-structured carbon frame materials is beneficial for the rapid diffusion of electrolytes, which effectively alleviate the volume changes during the electrochemical reaction process. Simultaneously, it can bring more active storage sites in the composites. [10,21–24]. For instance, Liu's group employed ZIF-67 as a template for the first time to design CoP nanoparticles embedded in nitrogen-doped carbon (NC). It delivered a high reversible discharge special capacity of $522.6 \text{ mA h g}^{-1}$ at 200 mA g^{-1} after 750 cycles and outstanding cycling stability up to 2000 cycles at 500 mA g^{-1} [10]. Li and his co-workers investigated the electrochemical properties of cage-structured CoP@N, P-doped double carbon from the confined phosphorization of ZIFs@CNCs, demonstrating a high initial columbic efficiency (ICE) of 96% and a superior cycle performance ($1215.2 \text{ mA h g}^{-1}$ after 1000 cycles at 200 mA g^{-1}) [19]. Although great achievements have been made in the synthesis of hollow-structured carbon-based CoP composite materials, more intensive studies are required to identify the relationship between the complex structures, controllable compositions, and the improvement of lithium storage.

As recently as the last century, it has been generally accepted that doping an appropriate amount of rare earth elements on the micro-nanostructured materials is a facile strategy to tune their morphology and electronic structures [18,25–27]. The addition of some dopant in the CoP lattices would lead to some defects, which are suitable for higher ionic conductance than that of undoped CoP materials. Rare earth elements, with their large radius, high charge, and 4f electron orbit, are expected to bring further improvements in LIBs. For example, Cerium (Ce) or Rubidium (Ru) doped into CoP used as hydrogen evolution reaction (HER) materials could promise its Pt-like HER catalytic performance by remarkably reducing the hydrogen binding energy and modulating their electronic structures and electronic conductivity [28,29]. Ce, benefiting from the strengths of the most abundant rare earth element and unique properties of a half-full 4f electron orbit, has been widely used to improve the mechanical stability and electronic conductivity in electrocatalysis and LIBs [25,30–33]. The hierarchy on hollow, polyhedron structural, doping of rare earth elements and the complementary effects between different ions determine the functionalities and performances of the materials. Therefore, the control of the hierarchy at each level is crucial [34–37].

In this work, the hollow polyhedron structured Ce-doped CoP@NC composites were rationally designed via chemical etching of ZIF-67 polyhedron with $\text{Ce}(\text{NO}_3)_3$ following a phosphorization procedure via gas-solid reactions. The as-prepared Ce-doped CoP@NC hollow polyhedron materials exhibited good cycle stability, which is comparable to that of CoP@NC.

2. Materials and Methods

2.1. The synthesis of Hollow Polyhedron Structured Ce-CoP@NC Composite

ZIF-67 polyhedrons were synthesized using a previously reported [10]. In the typical procedure, 5 mmol of $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 20 mmol of 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$) were dissolved in 30 mL of methanol, respectively. Then, the clear solution of $\text{C}_4\text{H}_6\text{N}_2$ was quickly poured into the clear solution of $\text{Co}(\text{NO}_3)_3$ while stirring vigorously for 1 h. Then, it was aged in atmosphere for 24 h. In the end, the product was collected by centrifugation, washed with methanol three times, and dried at 60°C for 4 h.

First, 0.2 g ZIF-67 powder was dispersed in 25 mL methanol under ultrasonication to obtain a homogeneous dispersion. Then 0.2 g (0.5 mmol) $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to the above dispersion. After stirring at room temperature for 12 h, the Ce-doped ZIF-67 precursor was formed and dried. The obtained product was put into a tube furnace and calcined at 600°C for 2 h in a nitrogen atmosphere with a heating rate of 2°C min^{-1} . Then, the Ce-Co/NC product was obtained.

Ce-CoP@NC was synthesized via a phosphidation process with NaH_2PO_2 as the phosphorus source. The Ce-Co@NC product and NaH_2PO_2 (a mass ratio of 1: 5) were put into two separate quartz boats. The quartz boat for NaH_2PO_2 was placed in the position of direction with gas entry in a tube furnace. Afterward, the material was calcined in N_2 atmosphere at $350\text{ }^\circ\text{C}$ for 2 h with $2\text{ }^\circ\text{C min}^{-1}$. Finally, Ce-CoP@NC was obtained.

2.2. Materials Characterization

The phase structures of the sample were determined using a Rigaku SmartLab (9) with Cu Ka radiation. The morphology and microstructures were characterized by scanning electron microscopy (SEM, JEOL-JSM-6700F) and transmission electron microscopy (TEM, FEI-Talos F200X) equipped with an aberration-corrector for the imaging lenses for high-resolution TEM (HRTEM), a high-angle annular dark-field (HAADF) detector for STEM, and an energy dispersive X-ray (EDX) detector for composition mapping. X-ray photoelectron spectroscopy (XPS) was performed by the Thermo Fisher Scientific ESCALAB Xi+ to determine the composition of samples. Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA 851 thermal analyzer with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under N_2 atmosphere. The specific surface areas of the samples were evaluated by using the Brunauere Emmette Teller test (BET, micromeritics-ASAP2460).

2.3. Electrochemical Measurements

The electrochemical tests were measured on a Land battery test system (CT2001A, Wuhan, China) at room temperature. The working electrodes were fabricated by pasting the mixed slurry that consisted of active materials (70 wt%), acetylene black (20 wt%), and sodium carboxy methyl cellulose (CMC, 10 wt%) onto a copper foil. The electrodes were dried at $80\text{ }^\circ\text{C}$ for 6 h in a vacuum oven. The final loading of the active materials for each electrode was about $0.8\sim 1.0\text{ mg cm}^{-2}$. The separator was a Celgard 2500 microporous polypropylene membrane. The residual space of the battery was filled by the nickel foam (7 mm in radius, $\sim 2\text{ mm}$ in thickness). The electrolyte used in the cells was 1 M LiPF_6 in an ethylene carbonate/diethyl carbonate containing fluoroethylene carbonate (EC/DEC = 1:1 v/v + 5% FEC). Lithium foil was used as a counter electrode. The coin cells of type CR2032 assembly were carried out in an argon-filled glove box with both the moisture and the oxygen content below 2 ppm. Galvanostatic discharge/charge cycled in the voltage range of $0.01\sim 3.0\text{ V}$ (vs. Li^+/Li). The cyclic voltammetry (CV) profiles and electrochemical impedance spectroscopy (EIS) were carried out by an electrochemical work station (Gamry reference 600+).

3. Results

3.1. Composition and Microstructures of the Composite Materials

The formation process of Ce-doped CoP@NC is schematically shown in Figure 1. Firstly, uniform polyhedral nanocrystals of ZIF-67 were synthesized with a typical method [10]. Then, through an ionic exchange experiment, the ZIF-67 particles were reacted with $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ to form the Ce-doped ZIF-67 precursor, without changing the uniform polyhedral shape of ZIF-67 particles. Subsequently, the as-prepared precursor composites were heated in a nitrogen atmosphere at $600\text{ }^\circ\text{C}$ for 2 h to transform Ce-doped ZIF-67 into Ce-doped Co@NC. In the final process, Ce-doped-CoP@NC hollow polyhedron composites were achieved through a phosphorization procedure via calcination treatment at $350\text{ }^\circ\text{C}$ for 2 h under a nitrogen atmosphere. Figure S1a,b (See Supplementary Materials) illustrate the X-ray diffraction (XRD) patterns of samples. After incorporating Ce ion into the ZIF-67 matrix, the obtained Ce-doped ZIF-67 exhibited a similar XRD diffraction pattern with ZIF-67 except the peaks shifted to larger angles. This phenomenon indicates that the Ce ion successfully inserted into the lattice structure of ZIF-67 and unchanged the crystal structure. The EDX elemental mapping image of the Ce-doped ZIF-67 shows the homogeneous distribution of Ce, Co, and C throughout the whole polyhedron (Figure S1c). The scanning electron microscopy (SEM) image of the Ce-doped ZIF-67 (Figure S2) illustrates it has a

smooth surface with rounded edges and corners (similar to the corresponding transmission electron microscopy (TEM) image in Figure 1) and without visible nanoparticles. The thermal behavior of Ce-doped ZIF-67 was investigated through the thermogravimetric analysis (TGA) method (Figure S3), which indicated that Ce-doped ZIF-67 underwent a weight loss lower than 600 °C and remained at 67% of its original weight when subjected to heat treatment under a flow of N₂. Therefore, we adopted a calcination process to pyrolyze Ce-doped ZIF-67 from room temperature to 600 °C at a ramping rate of 2 °C min^{−1}, and then stabilized at 600 °C for 2 h. The TEM bright-field (BF) image, high-angle annular dark-field (HAADF)-STEM image, and corresponding mapping images of Ce-doped Co/NC (Figure S4) indicated that Ce, Co, N, and C elements were uniformly distributed in the Ce-doped Co/NC hollow shell.

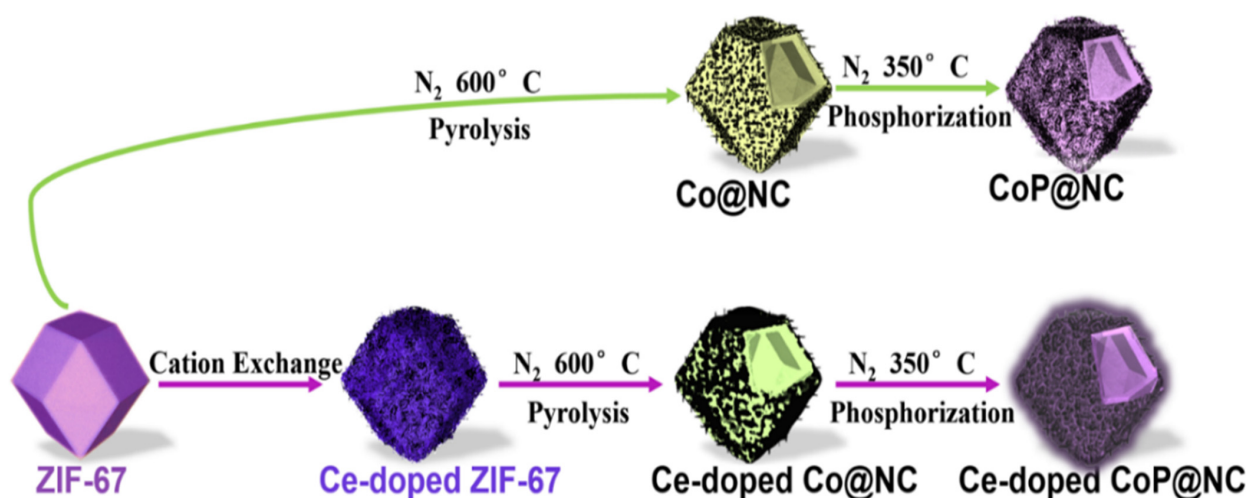


Figure 1. Schematic illustration showing the growth process of CoP@NC and Ce-doped CoP@NC hollow polyhedron.

Figure 2a shows the XRD patterns of the CoP@NC and Ce-doped CoP@NC samples. The diffraction peaks of the two samples were basically the same, which can be indexed as the orthorhombic CoP (JCPDS No. 29-0497). The broad diffraction peaks located at $\sim 26^\circ$ are well matched to amorphous carbon. It is worth mentioning that no XRD patterns related to CeO₂ species were observed. The enlarged views of XRD patterns are displayed in Figure 2b. It can be observed that the peaks at (011), (111), (112), and (211) of Ce-doped CoP@NC shifted to relatively lower angles compared with those of pristine CoP@NC. The phenomenon is due to the expansion of the lattice constant when the Co³⁺ (~ 0.58 Å) and Co²⁺ (0.65 Å) were partially substituted by Ce³⁺ with a larger radius for ~ 1.02 Å [29].

Figure 3 shows the X-ray photoelectron spectroscopy (XPS) of Ce-doped CoP@NC. From the full survey scan spectrum (Figure 3a), the Ce-doped CoP@NC sample consists of Co, Ce, P, C, and N elements, very compatible with the results of the XRD and elemental mapping. The high-resolution spectrum of Co 2p is presented in Figure 3b, which can be deconvoluted into two spin-orbit doublets. The first doublet centered at 782.3 and 784.0 eV are indexed to Co 2p_{3/2}. The second doublet located at 798.5 and 800.2 eV are identified to Co 2p_{1/2}. These peaks can be assigned to the Co element in Co-P and the surface cobalt oxide species. The peaks at 786.6 and 803.8 eV are the satellite peaks (denoted as “Sat”), which correspond to the Co²⁺ state. Besides, the peaks at 779.2 and 797.3 eV may be attributed to the presence of metallic Co in the composites [10,38–40]. In the Ce 3d spectrum (Figure 3c), two sets of spin-orbital multiples could be attributed to the Ce 3d_{5/2} and Ce 3d_{3/2}. The weak signals at 885.5 and 904.0 eV are the characteristic peaks of Ce-ion with the chemical valence of +3 [41–43]. Besides, there is no XPS pattern of CeO₂, which is in good agreement with the XRD results in Figure 2a. In the high-resolution curve of P 2p (Figure 3d), four peaks at 129.3, 130.2, 133.9, and 134.8 eV can be identified and assigned to the P 2P_{1/2}, P 2P_{3/2}, C-P bond, and O-P bond, respectively. The O-P bond might result

from the surface oxidation of the Ce-doped CoP@NC due to exposure to air. [10,44]. Similar to other carbonized ZIF structures, the N element originated from the high-temperature pyrolysis of nitrogen-rich 2-mIM. The N 1s spectra (Figure 3e) can be decomposed into three major peaks at binding energies of 401.6, 400.5, and 398.7 eV, which are attributed to the graphitic-N (N-C=C), pyrrolic-N (N=C), and pyridinic-N (N-H) in the composites, respectively. According to the previous reports, the incorporation of N atoms into carbon rings plays a key role in the charge delocalization of C atoms to improve the electrical conductivity and provides more lithium-active sites. Thus, the N-doped C will greatly improve the immobility of C, surface wettability, and stable electrode integrity. Thus, this reasonable design can effectively improve the stable cycle life of carbon-based materials for LIBs [45–47].

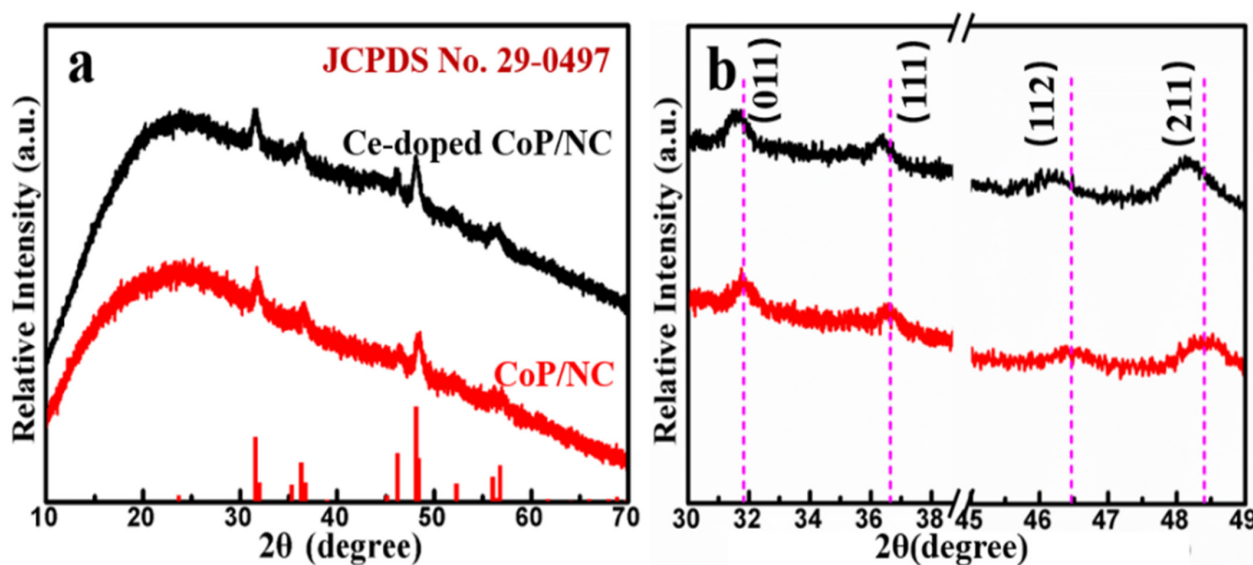


Figure 2. (a) XRD patterns, (b) the magnified diffraction peaks of the (011), (111), (112), and (211) of Ce-doped CoP@NC and CoP@NC.

Figure 4a,b show the typical SEM images of Ce-doped CoP@NC. After carbonization and phosphidation of Ce-doped ZIF-67, the irregular polyhedral structure was well-reserved with the size of about 600–1000 nm, with a slight surface shrinkage due to the decomposition process. Ce-doped CoP nanoparticles are embedded in an overlayer of the NC matrix. The TEM image (Figure 4c) of the Ce-doped CoP@NC displays it was an obvious hollow polyhedral structure. The SEM and TEM images of CoP@NC (Figure S5) show the hollow polyhedral structure with approximately 400–1000 nm. The curves exhibit the specific surface areas (BET) of CoP@NC and Ce-doped CoP@NC samples (Figure S6) are 55.467 and 96.848 $\text{m}^2 \text{g}^{-1}$, respectively. The hollow polyhedron structure and larger BET of Ce-doped CoP@NC facilitate the diffusion of electrolyte ions to the active sites and smart charge transport for reversible redox reactions, following an enhancement in lithium storage properties [46–48]. Based on the Barrett-Joyner-Halenda (BJH) plots, the corresponding pore size distributions are described in the inset of the Figure S6. They clearly illustrate that the Ce-doping resulted in a smaller pore size. The meso-sized pores in the Ce-doped CoP@NC provide optimal accessibility for transportation of electrolyte during LIB reaction. Figure 3d reveals that the Ce-doped CoP nanoparticles were surrounded by conductive carbon materials. The high-magnification HRTEM images (Figure 4e,f) display interlayer distances of around 0.247 and 0.350 nm corresponding to the (111) planes of CoP and (200) planes of amorphous carbon, respectively. The selected area electron diffraction (SAED) pattern (Figure 4g) consists of four concentric diffraction rings that belong to (011), (111), (211), and (301) diffraction planes of the CoP phase. The elemental mapping images (Figure 4h) display the uniform distribution of five elements (Ce, Co, C, N, P). The successful phosphidation and presence of bimetallic Ce and Co in the Ce-doped CoP@NC

composites are worth noting. From the HAADF-STEM image (Figure S7a,b), the elemental mapping result for Ce element indicated its uniform distribution within the shells. Energy dispersive X-ray spectroscopy analysis (EDX) from Figure S6c revealed the content of Ce in Ce-doped CoP@NC at approximately 2.23%.

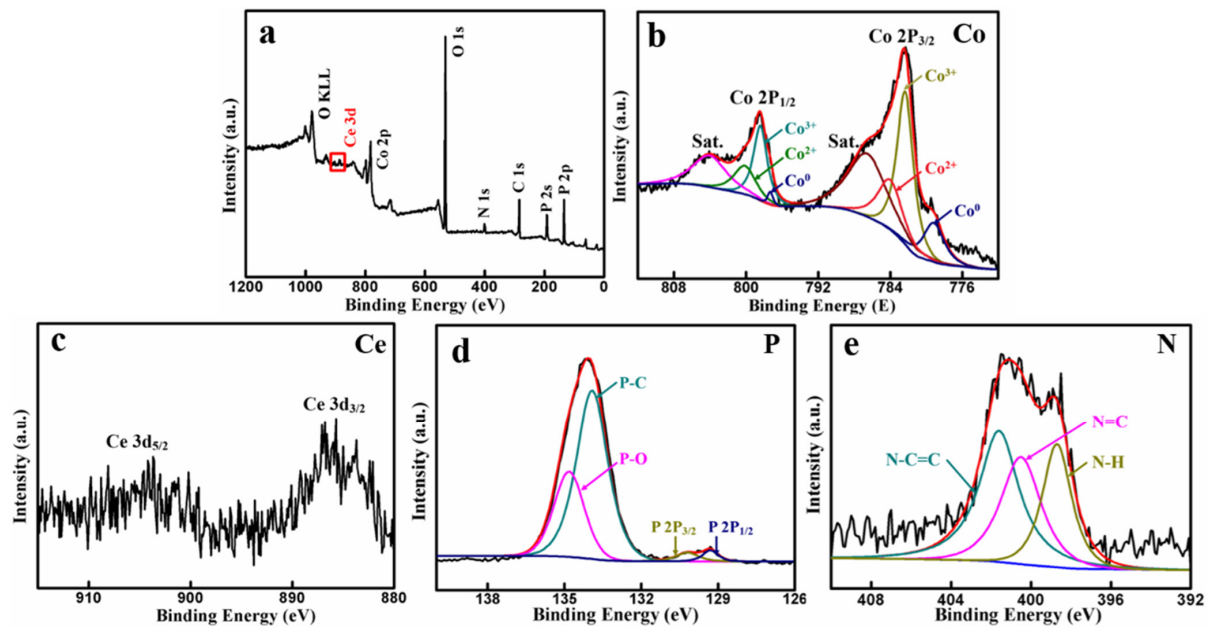


Figure 3. (a) XPS full spectrum, high-resolution XPS spectrum of (b) Co 2p, (c) Ce 3d, (d) P 2p, and (e) N 1s of Ce-doped CoP@NC.

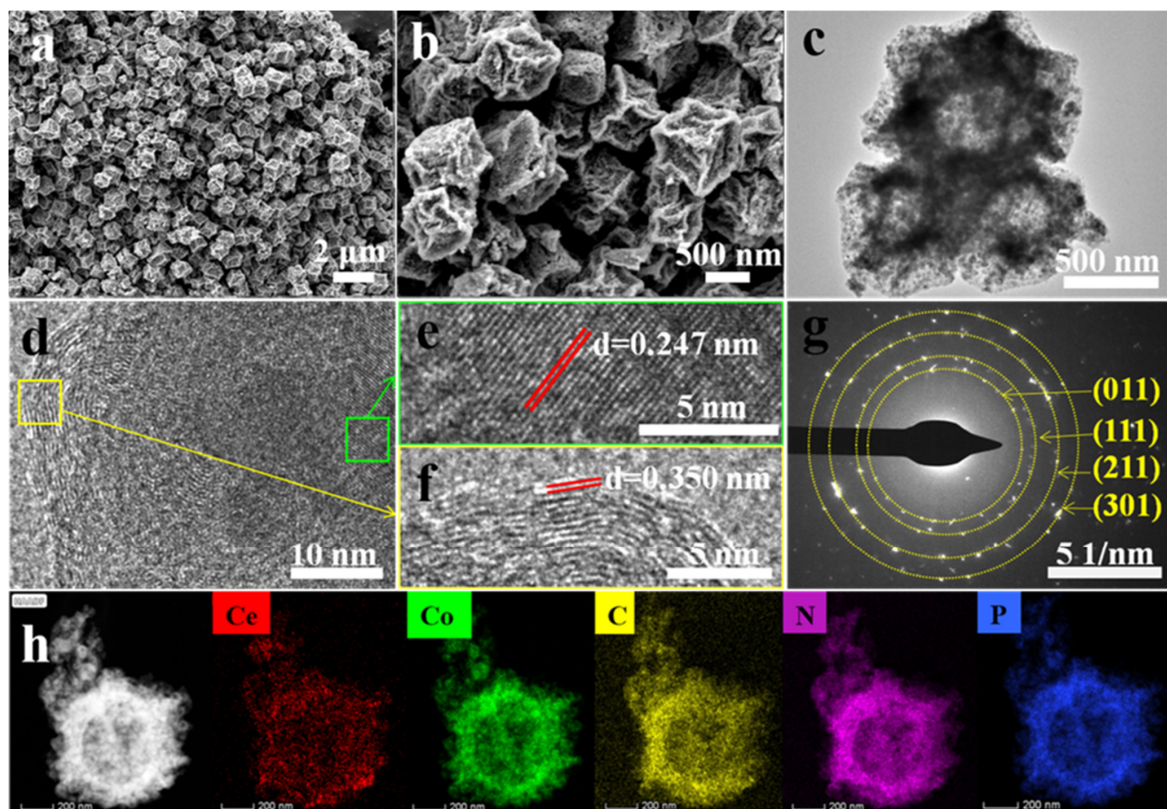


Figure 4. (a,b) SEM images, (c) TEM image, (d–f) HRTEM images, (g) selected-area diffraction pattern, and (h) EDX elemental mapping images of Ce-doped CoP@NC.

3.2. Electrochemical Property in Half-Cells

Cyclic voltammogram (CV) at a scan rate of 0.1 mV s^{-1} was used to investigate the electrochemical behavior of the Ce-doped CoP@NC anodes. As shown in Figure 5a, in the first cathodic scan, a major reduction peak at around 1.10 V corresponded to the conversion reaction of $\text{CoP} + 3\text{Li}^+ + 3\text{e}^- \rightarrow \text{Co} + \text{Li}_3\text{P}$ [18,21,47]. The small reduction peak near 0.47 V was assigned to some irreversible reaction together with the formation of the solid electrolyte interphase (SEI) film on the surface of electrode materials, which disappeared during the subsequent curves. This may result in capacity loss after the first cycle [10,47,49]. In the anodic peaks, approximately 1.05–1.16 V is attributed to the decomposition of Li_3P ($\text{Li}_3\text{P} \rightarrow \text{LiP} + 2\text{Li}^+ + 2\text{e}^-$). For the subsequent scans, the reduction peak at 1.10 V shifted to 0.60 V, which may be related to the activation and redistribution of CoP in the initial cathodic scan, as reported in the literature [50]. These peaks after the first scan became steady, revealing the highly electrochemical reaction reversibility of Ce-doped CoP@NC during the repeated Li^+ intercalation-deintercalation process. Figure 5b demonstrates the galvanostatic discharge and charge curves of Ce-doped CoP@NC for different cycles. Two discharge platforms and one discharge platform were visualized for the first cycle, which is consistent with the first CV curve. In the subsequent cycles, the curves almost overlapped even for the 50th cycle. It indicated the Ce-doped CoP@NC electrode possesses superior cyclability and reversibility. Figure 5c exhibits the galvanostatic cycling measurements of the Ce-doped CoP@NC electrode at 100 mA g^{-1} . It exhibits an initial discharge and charge specific capacity of 1229 and 741 mA h g^{-1} with an ICE of 60.3%. In the initial 20 cycles, the specific capacity slightly declined, which may be attributed to the gradual activation process, including the phase and structure transformations and the surface SEI film [18,31]. Subsequently, the specific capacity stabilized around 675 mA h g^{-1} . Additionally, the electrode performed more outstanding rate capabilities.

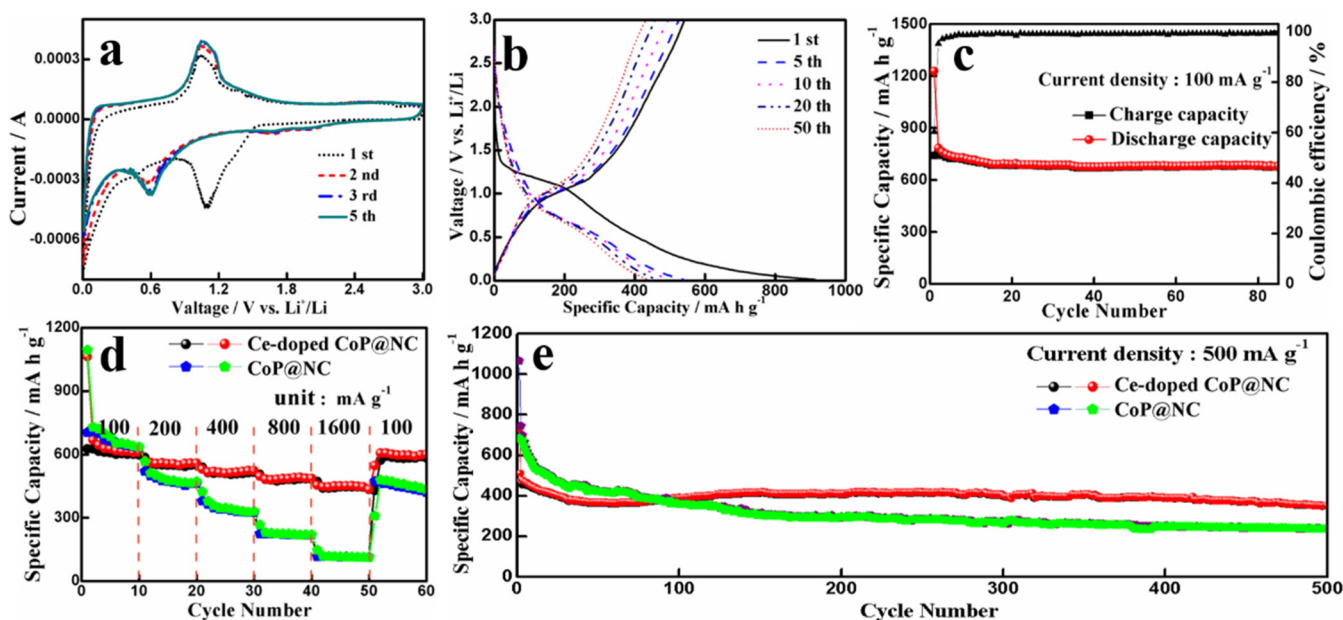


Figure 5. Electrochemical characterization for lithium storage electrodes. (a) CV of Ce-doped CoP@NC at a scan rate of 0.1 mV s^{-1} in the voltage range of 0.01–3.0 V. (b) Galvanostatic discharge and charge curves of Ce-doped CoP@NC for different cycles. (c) Cyclic behavior of Ce-doped CoP@NC. (d) Rate capabilities of Ce-doped CoP@NC and CoP@NC at different current densities. (e) Long-term cycling performance of Ce-doped CoP@NC and CoP@NC at 500 mA g^{-1} .

Figure 5d compares the rate capability of Ce-doped CoP@NC and CoP@NC electrode at varied current densities from 100 to 1600 mA g^{-1} . The average reversible discharge specific capacities of Ce-doped CoP@NC were 620, 560, 510, 480, and 440 mA h g^{-1} at

the increasing current of 100, 200, 400, 800, and 1600 mA g⁻¹, respectively. Furthermore, when the current density was reverted to 100 mA g⁻¹, the specific capacity could return to 590 mA h g⁻¹. However, the pure CoP@NC electrode exhibited inferior rate performance. At rates of 100, 200, 400, 800, and 1600 mA g⁻¹, it presented reversible capacities of 660, 470, 330, 230, and 125 mA h g⁻¹, respectively. When the rate returned to 100 mA g⁻¹, the specific capacity decayed rapidly to 450 mA h g⁻¹. To further evaluate the high-rate and long-term cycling stability, the Ce-doped CoP@NC and pure CoP@NC electrodes were cycled at a high current density of 500 mA g⁻¹ (Figure 5e). It can be intuitively observed that the discharge specific capacity of Ce-doped CoP@NC gradually tended to be stable and maintained a discharge specific capacity of ~400 mA h g⁻¹ after 500 cycles. The cycling stability of pure CoP@NC was rather poor, only retaining capacity of ~250 mA h g⁻¹ after 500 cycles. Therefore, ion doping might strengthen the structural integrity and stability of the electrode under high current densities [18,31].

To further investigate the charge transfer kinetics behavior of the electrode, electrochemical impedance spectroscopy (EIS) was studied. Figure S8 displays the Nyquist plots and the inset presents the corresponding equivalent circuit. In the Nyquist plots, the intercept on the X-axis in the high-frequency region corresponds to the electrolyte resistance (R_s); the diameter of the semicircle in the high/medium-frequency region is indexed to the charge-transfer resistance (R_{ct}) and the double-layer capacitance of the constant phase element (CPE), which occurs at the electrode/electrolyte interfaces; the slope of the inclined line in the low-frequency region corresponds to the Warburg impedance (Z_w) induced by the diffusion impedance of Li⁺ intercalation/deintercalation into the active anode [18,51]. As expected, the R_s and R_{ct} value of Ce-doped CoP@NC electrode was about 6.3 and 81.5 Ω , which is smaller than that of pure CoP@NC. All these explicitly designated that the introduction of Ce-ion could induce fast diffusion of Li⁺ and active sites for rapid ion diffusion.

4. Conclusions

In conclusion, the Ce-doped CoP@NC hollow polyhedron composites with a good lifespan and rate capability were successfully fabricated by the ionic-exchange, carbonization, and phosphorization methods. Ce-doped CoP nanoparticles were embedded in the NC hollow polyhedron skeleton. This unique nanoarchitecture and compositional merits can effectively hamper aggregation and buffer the volumetric expansion of CoP nanoparticles, fully immerse the structure in the electrolyte, and provide ample active sites for Li⁺ insertion and fast transport paths for ion/electron during cycling. As a result, the Ce-doped CoP@NC electrode exhibited high reversible capacity (690 mA h g⁻¹ at 100 mA g⁻¹) and excellent cyclability (the capacity of ~400 mA h g⁻¹ is maintained at 500 mA g⁻¹ after 500 cycles) for LIBs. We believe that the rare earth metal ion doping for M_xP_y is a promising and capable LIBs anode material for good rate capability and excellent cycling stability.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst12040533/s1>, Figure S1: (a) XRD patterns of ZIF-67 and Ce-doped ZIF-67. (b) the magnified region of $2\theta = 16.7\text{--}18.0^\circ$ showing a peak shift. (c) EDX elemental mapping images of Ce, Co and C for Ce-doped ZIF-67; Figure S2: SEM images of Ce-doped ZIF-67; Figure S3: The TGA curves of Ce-doped ZIF-67; Figure S4: (a) TEM bright field (BF) image, (b) HAADF-STEM image of Ce-doped Co/CN; Figure S5: (a,b) SEM images and (c,d) TEM images of CoP; Figure S6: N₂ adsorption/desorption isotherm of (a) CoP@NC and (b) Ce-doped CoP@NC; Figure S7: (a,b) HAADF-STEM images and (b) EDX analysis of Ce-doped CoP@NC; Figure S8: Nyquist plot and equivalent circuit model of Ce-doped CoP@NC and pure CoP@NC electrodes.

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