Direct Electrophoretic Deposition of Binder-Free Co₃O₄/Graphene Sandwich-Like Hybrid Electrode as Remarkable Lithium Ion Battery Anode

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Supporting Information

ABSTRACT: Co₃O₄ is emerging as a promising anode candidate for lithium ion batteries (LIBs) with high theoretical capacity (890 mAh g^{-1}) but suffers from poor electrochemical cycling stability resulting from the inferior intrinsic electronic conductivity and large volume changes during electrochemical cycling. Here, a new electrophoretic deposition Co_3O_4 /graphene (EPD Co_3O_4/G) hybrid electrode is developed to improve the electrochemical performance. Through EPD, Co3O4 nanocubes can be homogeneously embedded between graphene sheets to form a sandwich-like structure. Owing to the excellent flexibility of graphene and a large number of voids in this sandwich-like structure, the structural integrity and unobstructed conductive network can be maintained during cycling. Moreover, the electrode kinetics has proved to be a fast surface-controlled lithium storage process. As a result, the Co_3O_4/G hybrid electrode exhibits high specific capacity and excellent electrochemical cycling performance. The Co₃O₄/G hybrid electrode was also further



studied by in situ electrochemical XRD to understand the relationship of its structure and performance: (1) The observed $Li_xCo_3O_4$ indicates an intermediate of possible small volume change in the first discharging. (2) The theoretical capacity achievement of the Co_3O_4 in hybrid electrode was evidenced. (3) The correlation between the electrochemical performance and the structural evolution of the Co₃O₄/G hybrid electrode was discussed detailedly.

KEYWORDS: Co₃O₄, graphene, binder-free anode, electrophoretic deposition, lithium ion battery, in situ electrochemical XRD

1. INTRODUCTION

Lithium ion batteries (LIBs) have become the dominant power source in many consumer electronic devices since its successful commercialization by Sony Corporation in 1991.¹ However, with the increasing demand for large-scale energy storage applications such as smart grid and electric vehicles, developing new LIBs with higher power density is very imperative.² The anode is an indispensable component in LIBs, but the commonly used graphite anode suffers from its low theoretical specific capacity (only 372 mAh g^{-1}).³ Thus, the development of high-capacity anode materials is a crucial point to realize the greatest potential of the next generation LIBs.

Co₃O₄ is emerging as a promising anode candidate for LIBs with a much higher theoretical capacity (890 mAh g^{-1}) by reaction of its 8 electrons compared with the capacity of graphite.⁴ Nevertheless, Co₃O₄ anodes still face some limitations such as inferior intrinsic electronic conductivity and large volume changes during charging/discharging processes, which result in poor cycling stability and rate performance.

To date, two typical strategies have been proposed to solve these problems individually. One effective method is to construct nanostructured Co3O4 such as nanocubes,⁶ nanobundles,⁷ nanoflakes,⁸ hollow nanoparticles,⁹ and nanofibers,¹⁰ and so on, because nanostructures can alleviate the structural strain caused by volume changes of $\mathrm{Co}_3\mathrm{O}_4$ and provide reduced diffusion paths for Li^{+, 11,12} However, this design still fails to enhance the electrons transport. Another approach is to integrate Co₃O₄ with various carbon-based materials such as carbon nanotube,^{13,14} amorphous carbon,⁹ and carbon nanofiber,¹⁵ to improve the electronic conductivity. Graphene is regarded as the most appealing conductive carbon matrix owing to its excellent flexibility, fast electron mobility (2000 S cm⁻¹), and high theoretical specific surface area (over 2630 m² g⁻¹).¹⁶ Some previous reports have proved that graphene not only enhances the electronic conductivity but also serves as a buffer to relieve volume changes of Co_3O_4 .^{17–19} Thus, the $Co_3O_4/$ graphene composite design is one of the most effective choices to improve the electrochemical performance of Co₃O₄. In contrast, most Co₃O₄/graphene composites need to experience a complex process in the conventional electrode preparation method that involves the slurry mixture of active materials, conductive additives, and polymer binders in a solvent, then tape-casting the slurry onto a current collector. However, the

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Figure 1. (a) Schematic illustration for the fabrication procedures of the $Co_3O_4/graphene$ hybrid electrode. Photographs of (b) Co_3O_4/G hybrid electrode on the surface, (c) curved Co_3O_4/G hybrid electrode, and (d) Co_3O_4/G hybrid film deposited on the irregular substrates.

indispensable binder may aggravate the agglomeration of nanosized active materials in slurry mixture, which may damage the pristine structure of the composite material. Moreover, the conductive additives and binders used in the electrode will increase the extra weight and decrease the energy density of the actual battery.^{20,21}

In this work, we have developed a one-step multipurpose strategy to fabricate sandwich-like $Co_3O_4/graphene$ (Co_3O_4/G) hybrid electrode directly by using the electrophoretic deposition (EPD) method followed by heat treatment. Owing to the specific architecture, the as-prepared Co_3O_4/G hybrid

electrode exhibits advantageous characteristics: (1) Co_3O_4 nanocubes are homogeneously embedded between graphene sheets to form a sandwich-like structure, and the large number of voids formed in this hybrid film can provide buffer space for huge volume expansion of material during cycling. (2) Flexible graphene serves as a conductive matrix to improve the electronic conductivity and structural integrity in the electrode. (3) No binders and conductive additives are needed for the fabrication of Co_3O_4/G hybrid electrode, which is favorable to higher energy density and less agglomeration.²² As a result, the Co_3O_4/G hybrid electrode exhibits a more excellent electro-

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chemical performance than that of the Co_3O_4 electrode fabricated by the conventional slurry coating method. In addition, the EPD method shows the advantages of simplicity, low cost, and short fabrication time,^{23–26} suggesting that the Co_3O_4/G hybrid electrode can be a promising anode candidate for the next generation LIBs.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Co₃O₄ Nanocubes. Co_3O_4 nanocubes were prepared by further optimizing the previously reported hydrothermal method.^{6,27} Typically, 0.6 g of NaOH, 9 g of NaNO₃, and 17.4 g of $Co(NO_3)_2$ · $6H_2O$ were dissolved in 60 mL of deionized water and stirred for 30 min to form a homogeneous blue solution. Subsequently, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 5 h, followed by cooling to room temperature naturally. The black precipitate (Co_3O_4 nanocubes, shown in Figure S2) was obtained by centrifugation and washed with deionized water and ethanol for several times, then freeze-dried overnight.

2.2. Fabrication of the Co₃O₄/G Hybrid Electrode. First, 0.08 g of as-prepared Co₃O₄ nanocubes, 0.05 g of I₂, and 1.5 g of graphene NMP paste (1 wt %, Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, China) were added into 50 mL of acetone. The mixture was homogenized for 1 h by using the homogenizer (T10 basic, IKA Works GmbH & Co., Germany) to obtain an EPD suspension. As shown in Figure 1a, EPD was carried out under potentiostatic conditions by using a dc power supply (Xiamen Qunji Instrument Co. Ltd., China). The deposition substrate was Cu foil with a dimension of 2.0×2.5 cm², and the counter electrode was Pt foil with a dimension of 3.0×4.0 cm². The two electrodes were kept parallel at 1.5 cm apart in Teflon holders and inserted into the EPD suspension. After EPD at 100 V for 25 s, the deposition electrode was taken out and dried in a vacuum oven at 80 °C for 10 h. After annealing at 300 °C for 2 h with a heating rate of 5 °C min⁻¹ in Ar atmosphere, the final Co₃O₄/G hybrid electrode was obtained. The loading mass of the Co₃O₄/G composite film on the Cu foil was about 0.82 mg cm^{-2} .

2.3. Characterization. Zeta potential measurements were obtained from the Zetasizer instrument (90 Plus PALS, Brookhaven Instrument, USA). The X-ray diffraction (XRD) patterns were collected by using Rigaku Miniflex 600 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm). Thermogravimetric analysis (TGA) was carried out on TGA/DSC 1 STAR^e System (Mettler-Toledo, Switzerland) under air flow (30–800 °C, 10 °C min⁻¹). Raman spectra were measured on a Renishaw inVia Raman spectrometer (UK) with the laser wavelength of 532 nm. XPS tests were carried out on a Qtac-100 LEISS-XPS system. The morphology of the samples was investigated by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and high-resolution transmission electron microscopy (HRTEM, JEM-2100 and TECNAI G2 F30).

2.4. Electrochemical Measurements. The electrochemical properties were investigated by using CR-2016 type coin cells. The as-prepared Co₃O₄/G hybrid electrode can be directly used as the working electrode. The control Co₃O₄ electrodes were prepared by a conventional slurry coating method. First, 70 wt % Co₃O₄ nanocubes, 20 wt % acetylene black, and 10 wt % polyvinylidene fluoride (PVDF) were mixed in N-methyl-2-pyrrolidone (NMP) and stirred to make a slurry. The slurry was spread onto a Cu foil with an applicator and dried overnight at 80 °C in a vacuum oven. The half-cell for electrochemical test was assembled with Li metal as the counter and reference electrode, Celgard 2400 as the separator, and 1.0 M solution of LiPF₆ dissolved in the mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) (volumetric ratio of 1:1) as the electrolyte. The cells were evaluated using a charge/discharge unit (Neware BTS battery charger, Shenzhen, China) in the voltage range from 0.01 to 3.0 V at various current densities. Cyclic voltammetry (CV) was performed by using the CHI 1030C electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was carried out by the Autolab

Potentiostat Galvanostat 302N in the frequency range from 100 mHz to 100 kHz. All of the electrochemical tests were measured at 25 $^{\circ}$ C.

2.5. Characterization of *in Situ* Electrochemical XRD Measurement. The Co_3O_4/G hybrid film on the stainless-steel grid (the loading mass was around 2.1 mg cm⁻²) for *in situ* electrochemical XRD measurement was fabricated by the above EPD method. The assembling of modified coin cell for *in situ* electrochemical XRD measurement was schematically illustrated in Figure S1. The XRD pattern measurement and the galvanostatic charging and discharging were simultaneously performed on the modified coin cell. Every XRD pattern was measured simultaneously with galvanostatic charging and discharging (between 0.01 and 3.0 V at the current density of 0.066 A g⁻¹) on Rigaku Ultima IV by using Cu K α 0.154 nm X-ray radiation with X-ray power at 1200 W, 2 θ angle scanning at 2° min⁻¹, and step size of 0.02°.

3. RESULTS AND DISCUSSION

The EPD process is based on the migration and later deposition of charged particles in suspension, induced by the application of an electric field between two electrodes.²⁸ The migration process is considered as the "driven force", which can be described by the following equation:^{28–30}

$$\mu = \frac{E\varepsilon\varepsilon_0\zeta}{\eta} \tag{1}$$

where μ is the electrophoretic mobility, *E* is the applied electric field, ε is the dielectric constant of the dispersion medium, ε_0 is the permittivity of free space, ζ value is the zeta potential of the suspended particles, and η is the viscosity of the liquid. It can be seen that in a certain dispersion medium and electric field μ is mainly determined by the ζ value.²⁴

The EPD of two components on the substrate can be realized only as their ζ values are simultaneously positive or negative. As shown in Table 1, Co₃O₄ and graphene particles in

Table 1. Zeta Potentials (ζ) of Co₃O₄ and Graphene Suspended in Acetone with or Without I₂ Added

samples	ζ (mV)	ζ (mV), 1 mg mL ^-1 $\rm I_2$ added
Co_3O_4 (1.6 mg mL ⁻¹)	21.19	59.55
graphene (0.3 mg mL^{-1})	51.10	61.40

acetone are both positively charged, but the ζ of Co₃O₄ (21.19 mV) is too low to prepare a stable suspension. We choose I₂ as the dispersant. I₂ can react with acetone through the keto–enol reaction mechanism and produce protons, which can be absorbed to the surface of particles to enhance the amount of ionic charge.^{31,32} It can be seen that after I₂ is added the ζ of Co₃O₄ (59.55 mV) and graphene (61.40 mV) are increased and comparable. The as-prepared stable suspension is suitable for the EPD. Moreover, the residual I₂ can be easily removed through sublimation during the drying and annealing processes.³³

Figure 1b shows the photographs of the Co_3O_4/G hybrid electrode on the surface. The surface is uniform and smooth, and no exposure of the Cu foil and cracks are observed in the deposition region. After being curved, the composite film is capable of accommodating the bending of the Cu foil without the appearance of cracks, indicating the excellent adhesion between the composite film and the current collector (Figure 1c). Through EPD, the Co_3O_4/G hybrid film also can be deposited on the irregular substrates (Figure 1d), which is favorable to fabricate LIBs with different shapes or flexible LIBs. In addition, the Co_3O_4/G hybrid film deposited on the irregular



Figure 2. (a) XRD patterns (rhombuses marks indicate the Cu substrate) and (b) Raman spectra of the Co_3O_4 nanocubes and the Co_3O_4/G hybrid electrode. (c, d) SEM images and (e) element mapping of the Co_3O_4/G hybrid electrode on the surface. (f, g) SEM images of the Co_3O_4/G hybrid electrode on the cross section.

substrate (Figure 1d) was further straightened and distorted. It can be seen in Figure S3 that the Co_3O_4/G composite film neither fell off from the substrate nor cracked.

Figure 2a shows the XRD patterns of the pristine Co_3O_4 and the Co_3O_4/G hybrid electrode, assigned to the cubic $Fd\overline{3}m$ Co_3O_4 (Powder Diffraction File No. 42–1467, Joint Committee on Powder Diffraction Standards, 1990). The XRD peaks of Co_3O_4 in Co_3O_4/G hybrid electrode match well with those of pristine Co_3O_4 , indicating the undamaged Co_3O_4 crystal structure after EPD and heat treatment.

Raman spectroscopy was used to characterize the graphene in the Co_3O_4/G hybrid electrode (Figure 2b). The peaks of

pristine Co₃O₄ and Co₃O₄/G hybrid electrode before 800 cm⁻¹ are in good agreement with the feature of Co₃O₄ as previously reported.^{34,35} Four peaks located at 483, 521, 618, and 688 cm⁻¹ correspond to the E_g, F_{2g}, F_{2g}, and A_{1g} vibrational modes, respectively. The broad peaks of the Co₃O₄/G hybrid electrode at ~1359 and ~1592 cm⁻¹ are the characteristic D band (defect sites and disorders) and G band (graphite band) of carbon materials (arise from graphene).^{20,36,37} The small value of I_D/I_G (0.723) indicates the high quality of the graphene, which is appropriate to serve as a high-conductivity framework.^{38,39} The hybrid film was detached from the substrate by ultrasonic treatment in ethanol and dried to be used for the TG test. The



Figure 3. (a, b) TEM images, (c) SAED pattern, and (d) HRTEM image of the Co_3O_4/G hybrid. (e) High-angle annular dark field (HAADF) image and corresponding element mapping of the Co_3O_4/G hybrid. (f) HAADF image and corresponding line element analysis of the Co_3O_4/G hybrid.

result shows that the Co_3O_4/G hybrid film contains ~14.8 wt % carbon (Figure S4).

The Co₃O₄ nanocubes and graphene sheets in the EPD hybrid electrode can be clearly observed (Figure 2c) by SEM. The Co₃O₄ nanocubes can be distinguished through the transparent graphene layer (Figure 2d), indicating that most Co₃O₄ nanocubes are covered by quite thin graphene sheets and little graphene aggregation. The EDS mapping presents the uniformity of Co₃O₄ and graphene distribution across the electrode (Figure 2e). The Co_3O_4/G hybrid film on the Cu foil is ~18.2 μ m thick (Figure 2f). As shown in the highmagnification SEM image of the cross section, the Co₃O₄ nanocubes are sandwiched by graphene, where the graphene layer can be observed from its wrinkles (Figure 2g). The graphene layers not only prevent Co₃O₄ particles from aggregation but also help to form many small voids (Figure S5) which can buffer the volume change of the Co_3O_4 during electrochemical cycling.

The Co_3O_4/G hybrid film was detached from the substrate by ultrasonic treatment in ethanol and investigated by TEM. As shown in Figure 3a, even after ultrasonic treatment, the Co_3O_4 nanocubes are still tightly anchored to the graphene. From the high-magnification TEM image of a single Co3O4 particle (Figure 3b), we clearly observe that the Co_3O_4 nanocubes are decorated on the graphene surface. The SAED patterns of this region (Figure 3c) indicate that the Co_3O_4 nanocubes are single crystalline with [001] crystal planes exposed, and the faintness of the diffraction rings should be ascribed to the graphene. The HRTEM image (Figure 3d) demonstrates a typical Co₃O₄ nanocube wrapped by graphene sheets. The interplanar distance of the Co3O4 nanocube is ~0.28 nm, matching well with the cubic $Fd\overline{3}m$ Co₃O₄ (220) plane. The curved lattice fringes outside the Co₃O₄ nanocube may be assigned to graphene. The element mapping and line element analysis of C, Co, and O elements (Figure 3e,f) indicate that Co_3O_4

nanocubes are homogeneously anchored to the graphene sheets.

Electrochemical tests were performed on the assembled CR2016 half-cells to evaluate the electrochemical performance. Figure 4a presents the charge/discharge curves of the first two cycles of Co_3O_4 and Co_3O_4/G hybrid electrodes between 0.01 and 3.0 V at 0.2 A g^{-1} . An obvious voltage plateau at ~1.0 V is observed in the first discharge process of both samples, corresponding to the conversion from Co_3O_4 to Co; the slope region between 1.0 and 0.01 V may be ascribed to the formation of a polymer/gel-like film on the surface of formed Co nanoparticles (NPs).^{5,40} The initial discharge and charge capacities of the Co₃O₄/G hybrid electrode are 1303.9 and 946.0 mAh g^{-1} , corresponding to the initial Coulombic efficiency (CE) of 72.6%. For the contrastive Co_3O_4 nanocube electrode prepared by the conventional slurry coating method, the initial discharge and charge capacities are only 1231.4 and 733.3 mAh g^{-1} , corresponding to the lower initial CE of 59.6%. The improved initial CE may be attributed to the wellestablished conductive network in the EPD Co₃O₄/G hybrid electrode.

The electrochemical cycling performance of both samples at 0.2 A g^{-1} are shown in Figure 4b. For the EPD Co_3O_4/G hybrid electrode, a high reversible discharge capacity of 1113 mAh g^{-1} can be still maintained after 100 cycles, which is much higher than that of Co_3O_4 electrode (583 mAh g^{-1} after 50 cycles). Meanwhile, the CE of the EPD Co_3O_4/G hybrid electrode is retained above 98.7% steadily until the end of testing. High and stable CE means excellent reversibility of the conversion reactions between Li and Co_3O_4 .⁴¹ A rising trend of capacity is observed between cycles 3 and 75 for the EPD Co_3O_4/G hybrid electrode. It is probably originated from the following: (1) The gradual activation of Co_3O_4 grain boundaries increases surface area and active sites for lithium storage.⁴² (2) The continuous growth of polymer/gel-like film



Figure 4. (a) Charge/discharge curves of first two cycles and (b) electrochemical cycling performance of the Co_3O_4 and Co_3O_4/G hybrid electrodes at 0.2 A g⁻¹. (c) Rate performance of the Co_3O_4 and Co_3O_4/G hybrid electrodes at various current densities. (d) Nyquist plots and fitting results of the Co_3O_4 and Co_3O_4/G hybrid electrodes; inset is the equivalent circuit used for fitting. (e) Long-term electrochemical cycling performance of the Co_3O_4/G hybrid electrode at 1 A g⁻¹.

resulting from the decomposition of electrolyte provides pseudocapacitance capacity.^{43,44} Cycling performance of the Co_3O_4/G hybrid electrode with the higher loading mass of 1.24 mg cm⁻² has been also investigated (Figure S6).

Rate performance of both electrodes are displayed in Figure 4c. The Co_3O_4/G hybrid electrode exhibits an average discharge capacity of 993.5 mAh g⁻¹ at 0.1 A g⁻¹. As the current density increases to 0.2, 0.5, 1, 2, and 5 A g⁻¹, the average discharge capacity decreased gradually to 981.1, 941.3, 899.8, 819.5, and 687.7 mAh g⁻¹, respectively. Even at a much higher current density of 10 A g⁻¹, a reversible capacity of 358.2 mAh g⁻¹ can be also retained. When reducing the current density to 0.1 A g⁻¹ again, the discharge capacity raises to 1008 mAh g⁻¹ quickly, indicating the superior recovery of the Co_3O_4/G hybrid electrode. As a comparison, the Co_3O_4 electrode exhibits much inferior rate capability clearly. As the

current density increases to higher than 1 A g^{-1} , the specific capacity decreased to almost zero.

The long-term electrochemical cycling stability was further investigated (Figure 4e). The cells were activated at 0.2 A g⁻¹ for the first 5 cycles and cycled at 1 A g⁻¹ for all the subsequent cycles. After 750 cycles at a high current density of 1 A g⁻¹, the discharge capacity of the Co_3O_4/G hybrid electrode slowly decreases to 602.3 mAh g⁻¹, corresponding to an average capacity decay of only 0.038% per cycle. Meanwhile, the CE stayed at nearly 100% in the overall battery test, revealing the good cyclic stability and reversibility of the EPD Co_3O_4/G hybrid electrode.

Figure 4d shows Nyquist plots of the Co_3O_4 and EPD Co_3O_4/G hybrid electrodes, which can be further fitted by using the equivalent circuit (inset in Figure 4d). R_1 represents the electrolyte resistance, and R_f and R_{ct} are solid electrolyte interphase (SEI) film resistance and charge-transfer resistance,



Figure 5. (a) CV curves at various scan rates and (b) the relationship between the cathodic peak current and the scan rate for the Co_3O_4/G hybrid electrode. SEM images of (c, d) the Co_3O_4 electrode and (e, f) the Co_3O_4/G hybrid electrode after 50 cycles at 1 A g^{-1} . (g) Schematic illustration of structural change of the Co_3O_4/G hybrid electrode before and after lithiation.

respectively.⁴⁵ The detailed fitting results are shown in Table S1. Clearly, the $R_{\rm f}$ (15.15 Ω) and $R_{\rm ct}$ (58.72 Ω) of the Co₃O₄/G hybrid electrode are much smaller than that of the Co₃O₄ electrode (103.1 and 205.5 Ω , respectively).

In order to investigate the kinetic process, CV tests are carried out at various scan rates ranging from 0.2 to 3 mV s⁻¹. Due to the huge irreversible reactions, redox peaks of the Co_3O_4 electrode are hard to distinguish (Figure S7). While the CV curves of the EPD Co₃O₄/G hybrid electrode at different scan rates exhibit obvious and well-separated redox peaks (Figure 5a). For a redox reaction limited by semi-infinite diffusion, there is a power law relationship between peak current $(I_{\rm P})$ and the scan rate (v), $I_{\rm P} = av^{b.46,47}$ Thus, from the slope of the fitting line (Figure 5b), the power coefficient b is calculated to be 0.71, revealing that the electrode kinetics tends to be a surface-controlled lithium storage process.⁴⁸ It is wellknown that the surface-controlled lithium storage process is like supercapacitor behavior, benefiting the fast transport of Li⁺ ions.^{49,50} Thus, the smaller electrode-electrolyte resistance and quick surface-controlled kinetics of the Co₃O₄/G hybrid electrode are favorable for rapid charge and discharge.

The morphologies of both electrodes after 50 cycles at 1 A g^{-1} are also investigated. For the Co_3O_4 electrode, serious aggregation of Co_3O_4 nanocubes is observed (Figure 5d), and the huge mechanical stress induced by the volume change of Co_3O_4 leads to obvious cracks on the electrode surface (Figure 5c). However, the Co_3O_4/G hybrid electrode is basically intact and shows no obvious cracks (Figure 5e). The graphene sheets effectively relieve the aggregation of Co_3O_4 NPs (Figure 5f), ensuring the open paths of Li⁺ ions. The structural change of

the EPD Co₃O₄/G hybrid electrode is illustrated in Figure 5g. Owing to the excellent flexibility of graphene and many voids formed in the EPD Co₃O₄/G hybrid electrode, the graphene layers may effortlessly deform to accommodate the volume change of Co₃O₄ nanocubes and tightly connected to the Co₃O₄ nanocubes. Therefore, the EPD Co₃O₄/G hybrid electrode design can perform excellent structural integrity and unobstructed conductive network.

The electrochemical performance of metal oxide anodes are usually correlated with their structural evolution in the electrochemical reaction.^{51–53} It may help to improve the material structure design if the structural evolution of the material can be understood. The previous work also indicated that the structural evolution of Co_3O_4 was impacted by its particle texture, size, and other physical properties.⁵⁴ In this work, the Co_3O_4 nanocubes have very specific morphology, texture and crystallinity. The physical features of Co_3O_4 nanocubes in this work are quite different from those of the Co_3O_4 materials in previous reaction mechanism studies.^{54,55} Hence, it is necessary for us to probe the structural evolution of the Co_3O_4/G hybrid electrode to better understanding its electrochemical performance.

XRD technique is a very powerful tool for studying the crystal structure and can help us to understand the structural evolution of crystal materials in electrochemical reaction, ^{56,57} so the *in situ* electrochemical XRD was used to study the reaction mechanism of the single-crystalline Co_3O_4 nanocubes in the EPD hybrid electrode. The *in situ* electrochemical XRD patterns and the simultaneous galvanostatic discharging and charging curves are shown in Figure 6.



Figure 6. *In situ* electrochemical XRD patterns of the EPD Co_3O_4/G hybrid electrode: (a) voltage curves in the first electrochemical cycling of the EPD Co_3O_4/G hybrid electrode in *in situ* electrochemical XRD coin cell at 0.066 A g⁻¹. The graphene capacity shown in Figure S8 is negligible compared to the Co_3O_4 capacity, so the total capacity of the hybrid electrode can approximately be attributed to Co_3O_4 . The *x* in $Li_xCo_3O_4$ is calculated based on the Co_3O_4 quantity in the EPD Co_3O_4/G hybrid electrode); (b–i) simultaneous *in situ* XRD patterns corresponding to (a); intensity color bar is placed on the right, with intensity from 5000 to 11 600 cps for (b), (c), and (e–h), from 5000 to 21 200 cps for (d) and from 5000 to 10 000 cps for (i). Setting up different intensity scales for the colorbars of (b–i) is to make the XRD peaks of low intensity more distinct). The black dashed lines in (b–i) indicate the Co_3O_4 XRD peaks indexed as 111, 222, 400, and 440. The orange, red, and purple dashed lines indicate three stages in the first discharging process.



Figure 7. C 1s XPS spectra for (a) Co_3O_4/G hybrid electrode at the first lithiation state and (b) pristine Co_3O_4/G hybrid electrode.

From the pristine state to the orange dashed line (0 < x < 3)in Figure 6, the Co_3O_4 XRD peaks continuously shift to lower 2θ value, revealing the lattice expansion of the Co₃O₄ nanocubes. The lattice expansion may be related with the Li⁺ intercalation into the Co₃O₄ nanocubes. The Co₃O₄ XRD peaks also become weak and broad, indicating the evolution of pristine Co_3O_4 crystal structure. In the same time, when x > 1in discharging, the XRD peaks relative to the cubic spinel Li_rCo₃O₄ appear, which are shown in black dashed rectangles in Figure 6b,e,f,i. The assignment of XRD peaks relative to the $Li_xCo_3O_4$ can be supported by several previous works. (The x in 'Li_xCo₃O₄' only indicates the mole fraction of Li⁺ vs Co₃O₄ chemical formula. Li_xCo₃O₄ actually involves several intermediates and is not a definite substance, so Li_xCo₃O₄ only stands for the Li⁺-intercalated phase in this work.)^{54,55} The formation of Li_xCo₃O₄ further confirms the intercalation of Li⁺ into Co₃O₄ crystal. The Co₃O₄ phase is continuously transited into the Li_xCo₃O₄ phase until x > 3 as the orange line indicated.

When x > 8, as indicated by the red dashed line in Figure 6, the XRD peaks relative to $\text{Li}_x\text{Co}_3\text{O}_4$ nearly disappear. The $\text{Li}_x\text{Co}_3\text{O}_4$ XRD peaks disappearing may indicate the $\text{Li}_x\text{Co}_3\text{O}_4$ has totally conversed to Co and Li_2O because the observed experimental capacity is simultaneously in agreement with the theoretical capacity of Co_3O_4 . The simultaneous disappearance of $\text{Li}_x\text{Co}_3\text{O}_4$ XRD peaks and the theoretical capacity achievement may also indicate the capacity of Co_3O_4 nanocubes can be fully utilized by the binder-free EPD Co_3O_4/G hybrid electrode design. The additional single XRD patterns for some important intermediate phases of Co_3O_4 are also shown in Figure S9.

As reported in the previous work,⁵⁴ there are two reaction paths for Co3O4 of different physical features in the first discharging process: (a) $Co_3O_4 + Li^+ + e^- \rightarrow Li_xCo_3O_4$ and $\text{Li}_{x}\text{Co}_{3}\text{O}_{4} + \text{Li}^{+} + e^{-} \rightarrow \text{Co} + \text{Li}_{2}\text{O}_{3}(b) \text{Co}_{3}\text{O}_{4} + \text{Li}^{+} + e^{-} \rightarrow$ $CoO + Li_2O$ and $CoO + Li^+ + e^- \rightarrow Co + Li_2O$. Obviously, the Co_3O_4 nanocubes in hybrid electrode take reaction path (a). Reaction path (a) will produce the reaction intermediate of much less volume expansion than that of reaction path (b). The smaller volume expansion during the formation of intermediate phases in reaction path (a) may help to relieve the internal electronic contact loss problem of material particles in discharging. The $Li_xCo_3O_4$ intermediate phase may also decrease phase separation in the conversion reaction and keep the integrity of material particles, compared to the formation of CoO and Li₂O in reaction path (b) upon discharging. Therefore, the Li_xCo₃O₄ intermediate formed in structural evolution may indirectly help to stabilize the electrochemical performance of EPD Co₃O₄/G hybrid electrode in subsequent electrochemical cycles.

In Figure 6, the first discharging process of Co_3O_4 continues even after achieving the theoretical capacity, and the slope of

the discharging plateau (red to purple dashed lines) is quite different from that of the previous flat discharging process. The discharging capacity exceeding the theoretical capacity of Co_3O_4 is relative to SEI (solid electrolyte interface) film formation as the previous works reported.^{5,40}

To confirm the formation of SEI film after the third stage of the first discharging process in Figure 6, the XPS measurements have been carried out on the EPD Co_3O_4/G hybrid electrode at the first lithiated state (discharging to 0.01 V). For pristine EPD Co_3O_4/G hybrid electrode (Figure 7b), the C 1s spectrum can be deconvoluted into three peaks located at 284.8 eV (C–C), 285.8 eV (C–O), and 288.2 eV (C=O) attributed to the graphene. However, for EPD Co_3O_4/G hybrid electrode at the first lithiation state (Figure 7a), an additional peak at 290.0 eV relative to O=C–O contained species is observed, indicating ROCO₂Li in the SEI.

In the first charging process, the *in situ* electrochemical XRD patterns in Figure 6 show no obvious peaks, and this may be related with the amorphous state of cobalt oxides, Co and Li₂O, formed after the first discharging process. The similarity of the electrochemical behavior in subsequent electrochemical cycles after the first discharging process shown in Figure S10 may indicate that the amorphous cobalt oxides, Co and Li₂O, dominate the subsequent electrochemical cycles. This speculation can also be supported by the previous works relative to the conversion type metal oxide LIB materials.^{58,59}

On the basis of the *in situ* electrochemical XRD and *ex situ* XPS results, the reaction mechanism of EPD Co_3O_4/G hybrid electrode can be concluded as follows:

Lithiation in the first cycle:

 $Co_3O_4(crystalline) + xLi^+ + xe^- → Li_xCo_3O_4(crystalline)$ Li_xCo_3O_4(crystalline) + (8 - x)Li^+ + (8 - x)e^-→ 3Co⁰ + 4Li_3O

Delithiation in the first cycle:

 $3\text{Co}^{0} + 4\text{Li}_{2}\text{O} \rightarrow \text{Co}_{3}\text{O}_{4}(\text{amorphous}) + 8\text{Li}^{+} + 8\text{e}^{-}$

Lithiation/delithiation in subsequent cycles:

 $Co_3O_4(amorphous) + 8Li^+ + 8e^- \leftrightarrow 3Co^0 + 4Li_2O$

SEI film formation contributes to the capacity over the theoretical capacity of Co_3O_4 in the first lithiation process. The lithiation of Co_3O_4 contains both intercalation reaction and conversion reaction in the first electrochemical cycle. After the first electrochemical cycle, the crystalline Co_3O_4 turns to be amorphous. The subsequent electrochemical cycling after the first discharging is dominated by conversion reaction.

4. CONCLUSIONS

The binder-free Co_3O_4/G hybrid electrode with sandwich-like structure is successfully fabricated via a simple EPD strategy and subsequent heat treatment. Owing to the specific structural features of the EPD Co_3O_4/G hybrid electrode, excellent structural integrity, and unobstructed conductive network can be maintained during cycling. Moreover, the Co_3O_4/G hybrid film is proved to possess surface-controlled electrode kinetics and small charger-transfer resistance, permitting fast transport of Li⁺ ions and electrons. As a result, the EPD Co_3O_4/G hybrid electrode exhibits high specific capacity (1113 mAh g⁻¹ after 100 cycles at 0.2 A g⁻¹) and excellent long-term cyclic stability (602.3 mAh g⁻¹ after 750 cycles at 1 A g⁻¹, corresponding to an

average capacity decay of only 0.038% per cycle). By in situ electrochemical XRD and ex situ XPS results, we find the reaction mechanism of Co₃O₄ nanocubes contains both the Li⁺ intercalation process and conversion process in the first discharging process. The Li_xCo₃O₄ intermediate is observed in the Li⁺ intercalation reaction in the first discharging process. The existence of $Li_rCo_3O_4$ may be helpful to relieve the volume change problem and further stabilize the electrochemical cycling performance of Co₃O₄. The theoretical capacity of Co₃O₄ nanocubes can be achieved by the sandwich-like EPD Co_3O_4/G hybrid design. The SEI film will form after the Co_3O_4 theoretical capacity has been achieved. The subsequent electrochemical cycles after the first discharging process may be dominated by the conversion reaction. Since the outstanding advantages of scaling up capability, high efficiency, and low cost benefiting from the EPD technique, EPD Co₃O₄/G hybrid electrode can be a potential binder-free anode candidate for high-performance LIBs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b10683.

Configuration of the modified coin cell for in situ electrochemical XRD; SEM of the Co_3O_4 nanocubes and the voids formed in the Co_3O_4/G hybrid electrode; photographs of the Co_3O_4/G hybrid film deposited on the irregular substrate which has been straightened and distorted; TGA of the Co_3O_4/G hybrid film; cycling performance of the Co_3O_4/G hybrid electrode with the loading mass of 1.24 mg cm⁻²; equivalent-circuit parameters and corresponding fitting errors obtained from fitting the experimental impedance spectra; CV curves of the Co_3O_4 electrode; galvanostatic test curves of the graphene in the EPD Co_3O_4/G hybrid electrode; single XRD patterns for some important intermediate phases of Co_3O_4/G ; galvanostatic test curves of the Co_3O_4/G hybrid electrode in the multicycles (PDF)

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Y.Y. and J.H. contributed equally to the creation of this work. **Notes**

The authors declare no competing financial interest.

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32811