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## Nanoparticle Decorated Ultrathin Porous Nanosheets as Hierarchical $\text{Co}_3\text{O}_4$ Nanostructures for Lithium Ion Battery Anode Materials

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We report a facile synthesis of a novel cobalt oxide ( $\text{Co}_3\text{O}_4$ ) hierarchical nanostructure, in which crystalline core-amorphous shell  $\text{Co}_3\text{O}_4$  nanoparticles with a bimodal size distribution are uniformly dispersed on ultrathin  $\text{Co}_3\text{O}_4$  nanosheets. When tested as anode materials for lithium ion batteries, the as-prepared  $\text{Co}_3\text{O}_4$  hierarchical electrodes delivered high lithium storage properties comparing to the other  $\text{Co}_3\text{O}_4$  nanostructures, including a high reversible capacity of  $1053.1 \text{ mAhg}^{-1}$  after 50 cycles at a current density of  $0.2 \text{ C}$  ( $1 \text{ C} = 890 \text{ mAhg}^{-1}$ ), good cycling stability and rate capability.

Rechargeable lithium-ion batteries (LIBs) are one of the great successes of modern materials electrochemistry—used in electronics, mobile phones, and laptop computers<sup>1,2</sup>. High-performance LIBs with higher capacity, longer cycle life, and better rate capability have attracted considerable interests in the electric vehicle market and for implantable medical devices etc<sup>1–5</sup>. It is widely accepted that the overall performance of LIBs is highly dependent on the inherent electrochemical properties of the electrode materials<sup>6,7</sup>. Therefore, considerable attention has been paid to develop novel materials for both the cathodes and anodes of LIBs which are inexpensive, safe and environmentally benign. So far, various materials, such as graphitic/non-graphitic carbon<sup>8–10</sup>, transition-metal oxides<sup>11,12</sup>, nitrides<sup>13,14</sup>, phosphates<sup>15</sup>, lithium alloys<sup>16–20</sup> and their composites have been exploited as the anode materials of LIBs. Among them,  $\text{Co}_3\text{O}_4$  is a promising material for the LIB anode due to its high theoretical capacity ( $890 \text{ mAhg}^{-1}$ , according to the electrochemical reaction  $\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \leftrightarrow 3\text{Co} + 4\text{Li}_2\text{O}$ ). The capacity is more than two times larger than that of graphite ( $372 \text{ mAhg}^{-1}$ ), which is anticipated to meet the requirements of future energy storage systems<sup>21</sup>. Nevertheless, the main weakness of  $\text{Co}_3\text{O}_4$  anode materials for LIBs lies in the large volume expansion and severe particle aggregation associated with the  $\text{Li}^+$  insertion and extraction process, resulting in the deterioration of the reversible capacity and poor cycling stability<sup>21</sup>. Various strategies have been attempted to overcome these limitations and improve the performance. Design and synthesis of electrode materials with proper composition, morphology (such as nanopowders, nanowires, nanorods and nanotubes), and microstructure on the nanoscale is a time-tested route to enhance the lithium storage properties<sup>22–25</sup> (see  $\text{Co}_3\text{O}_4$  anode nanostructures overview in Table S1). Li *et al.*<sup>24</sup> synthesized self-supported mesoporous  $\text{Co}_3\text{O}_4$  nanowire arrays directly grown on Ti foil, which showed high capacity, good cyclability and high rate capability. Nam and Belcher *et al.*<sup>25</sup> used viruses to synthesize and assemble Au modified  $\text{Co}_3\text{O}_4$  nanowires at room temperature, and demonstrated the improved battery capacity when used as anodes for LIBs. Combining nanostructured electrode materials with electronically conductive agents, such as carbon nanofibers, carbon nanotubes, and graphene, is considered as another effective approach to improve the cycling stability and rate capability<sup>26,27</sup>. The conductive additives not only act as a “buffer zone” of volume variation induced by the cycling process but also a good

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electron transfer medium<sup>28–31</sup>. However, the addition of conductive agents unavoidably decreases the effective use of active materials.

Recent works show that three-dimensional (3D) complex hierarchical architectures assembled by low-dimensional nano-sized building blocks possess enhanced LIB performance<sup>32–34</sup>. For example, Sun and co-workers<sup>32</sup> developed a high-performance cathode material based on nickel-rich lithium transition-metal oxide with full concentration gradient within each particle, and the micrometre-size secondary particles of the material were composed of aligned needle-like nanosize building blocks. The developed material could deliver a specific capacity of up to 215 mAhg<sup>-1</sup> with outstanding cycling stability in a full-cell configuration, maintaining 90% capacity retention after 1,000 cycles. We previously reported a facile synthesis of 3D hierarchical porous Co<sub>3</sub>O<sub>4</sub> nanostructures with morphologies including hierarchical nanoflowers and hyperbranched nanobundles, which were all built up by numerous nanoparticles with random attachment. Of those, the nanoflowers demonstrated the highest performance as an anode materials for LIBs<sup>35</sup>.

Herein, we report a novel material based on crystalline core-amorphous shell nanoparticles decorating ultrathin nanosheets of hierarchical Co<sub>3</sub>O<sub>4</sub> nanostructures (Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN). In this structure, crystalline@amorphous core/shell Co<sub>3</sub>O<sub>4</sub> nanoparticles with a bimodal size distribution were decorated on ultrathin Co<sub>3</sub>O<sub>4</sub> nanosheets. When evaluated as an anode material for LIBs, the Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN delivered a reversible capacity of 1053.1 mAhg<sup>-1</sup> after 50 cycles at a current density of 0.2 C (1 C = 890 mA g<sup>-1</sup>), good cycling stability and rate capability. The lithium storage properties, especially the rate capacity of the current Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN were superior to the reported Co<sub>3</sub>O<sub>4</sub> nanostructures. The improved performance was ascribed to the unique designed nanostructured Co<sub>3</sub>O<sub>4</sub>.

## Results

The route to obtain Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN was adapted from our previously described synthesis of mesoporous Co<sub>3</sub>O<sub>4</sub> nanosheets with some modifications (see the Supporting Information (SI) for details). Briefly, the cobalt hydroxide sheet precursors were obtained by reacting Co(OH)<sub>2</sub>·6H<sub>2</sub>O, hexamethylenetetramine, and water at 95 °C for 8 h. The product was then annealed at 450 °C in air for 2 h to form Co<sub>3</sub>O<sub>4</sub> nanosheets that have previously been investigated<sup>36</sup>. In the last step, the annealed samples were soaked in NaBH<sub>4</sub> solution for an hour to yield C@A NPs-NSs HN.

The morphology of the as prepared precursors shows sheet-like character (Fig. S1a, Supporting Information). EDX pattern confirms the composition of the precursor (Fig. S1a inset, SI). Powder X-ray diffraction (XRD) result indicates all the diffraction peaks can be indexed as Co(OH)<sub>2</sub> (JCPDS No. 74–1057) (Fig. S1b, SI). The thermal behavior of the Co(OH)<sub>2</sub> precursor is studied by TG analysis (Fig. S2, SI). From the TGA curve measured under air atmosphere, it can be clearly seen that the weight loss takes place in the temperature range 50–220 °C, and it is mainly attributed to the removal of physically adsorbed water and partial decomposition of the solid precursor into Co<sub>3</sub>O<sub>4</sub> nanosheets. After reaching 250 °C, the weight loss drops sharply to about 30%. Then the weight loss is gradual and finally it flattens at 350 °C. On the basis of these results the as-synthesized precursors were annealed at 450 °C. The structure and morphology characterizations indicate that the annealed products are phase pure Co<sub>3</sub>O<sub>4</sub> with mesoporous nanosheets (Co<sub>3</sub>O<sub>4</sub> mNSs) nature (Figs S3 and S4, SI).

The final Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN can be obtained by soaking the annealed Co<sub>3</sub>O<sub>4</sub> mNSs in NaBH<sub>4</sub> solution for an hour. The crystallographic structure of Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN are checked by XRD as shown in Fig. 1. All the diffraction peaks can be assigned to (220), (311), (222), (400), (422), (511), (440), (620) and (533) planes of Co<sub>3</sub>O<sub>4</sub> (JCPDS No. 74–1657, a = 8.0837 Å). No other diffraction peaks from possible impurities are observed, indicating the high phase purity of the Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN. The diffraction peaks for Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN are not as sharp as that of starting Co<sub>3</sub>O<sub>4</sub> mNSs, implying the crystallinity of Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN is reduced after soaking in NaBH<sub>4</sub> solution.

The morphology of Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN is examined by field emission scanning electron microscopy (FESEM) as shown in Fig. 2. It can be seen that the surface of Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN is coarse and shows wrinkled morphology (Fig. 2a,b), in sharp contrast with that for Co<sub>3</sub>O<sub>4</sub> mNSs (Fig. S4a, SI). An enlarged FESEM image (Fig. 2c) clearly shows that numerous Co<sub>3</sub>O<sub>4</sub> nanoparticles are uniformly distributed on the surface of the nanosheets. A higher magnification FESEM image shows that two kinds of Co<sub>3</sub>O<sub>4</sub> nanoparticles (small size and large size) are observed on the surface (Fig. 2d and the inset). The average diameters of the two kinds of nanoparticles are ~6 and ~45 nm, respectively. Although various 0D nanoparticles (metal, metal oxides/sulfide/nitrides) have been successfully deposited on 2D nanosheets (such as graphene, reduced graphene oxide, layered transition metal dichalcogenide nanosheets, atomically-thick nanosheets with non-layered structure, and so on)<sup>27,37–39</sup>, to the best of our knowledge, this is the first report on the synthesis of 0D–2D hybrid nanostructures for a given material via a facile solution method.

The detailed structural investigations of Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN are studied by TEM and HRTEM. Figure 3(a–d) are typical TEM images of Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN with different magnifications; it can be seen that the hierarchical nanosheets are highly porous (Fig. S5a,b). The sheets are folded in some locations and the dark regions are the result of overlapping of sheets. Moreover, the porous nanosheets are decorated with high-density nanoparticles. A bimodal size distribution with mean diameters of ~5.5 nm and ~43 nm are obtained by analyzing over 200 nanoparticles for the sample (the inset in Fig. 3b). The results are in good agreement with the above FESEM observations. A selected area electron diffraction pattern (Fig. 3c inset) clearly demonstrates the polycrystalline nature of Co<sub>3</sub>O<sub>4</sub> C@A NPs-NSs HN, which is consistent with the XRD results.

EDS mapping analysis indicates the uniform distribution of cobalt and oxygen in the product (Fig. 3e), confirming the composition of supported Co<sub>3</sub>O<sub>4</sub> nanoparticles as well. The HRTEM image of an individual Co<sub>3</sub>O<sub>4</sub> nanosheet from the hierarchical nanostructures is shown in Fig. 3(f). The distinct lattice spacing is measured to be ~4.70 Å, which corresponds to the (111) plane of Co<sub>3</sub>O<sub>4</sub>. HRTEM image shown in Fig. 3(g) illustrates that the Co<sub>3</sub>O<sub>4</sub> nanoparticles are supported on the nanosheets. The nanoparticles possess unique crystalline

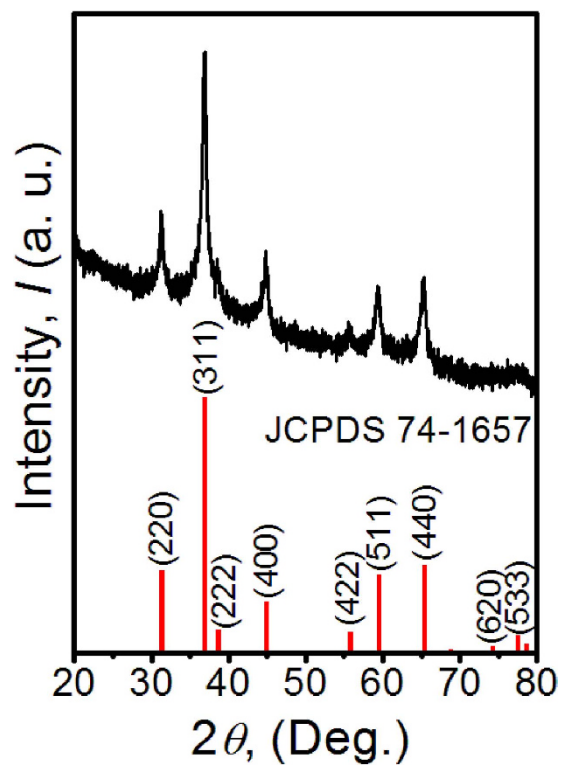


Figure 1. XRD pattern of as-prepared sample and the standard pattern of Co<sub>3</sub>O<sub>4</sub> phase.

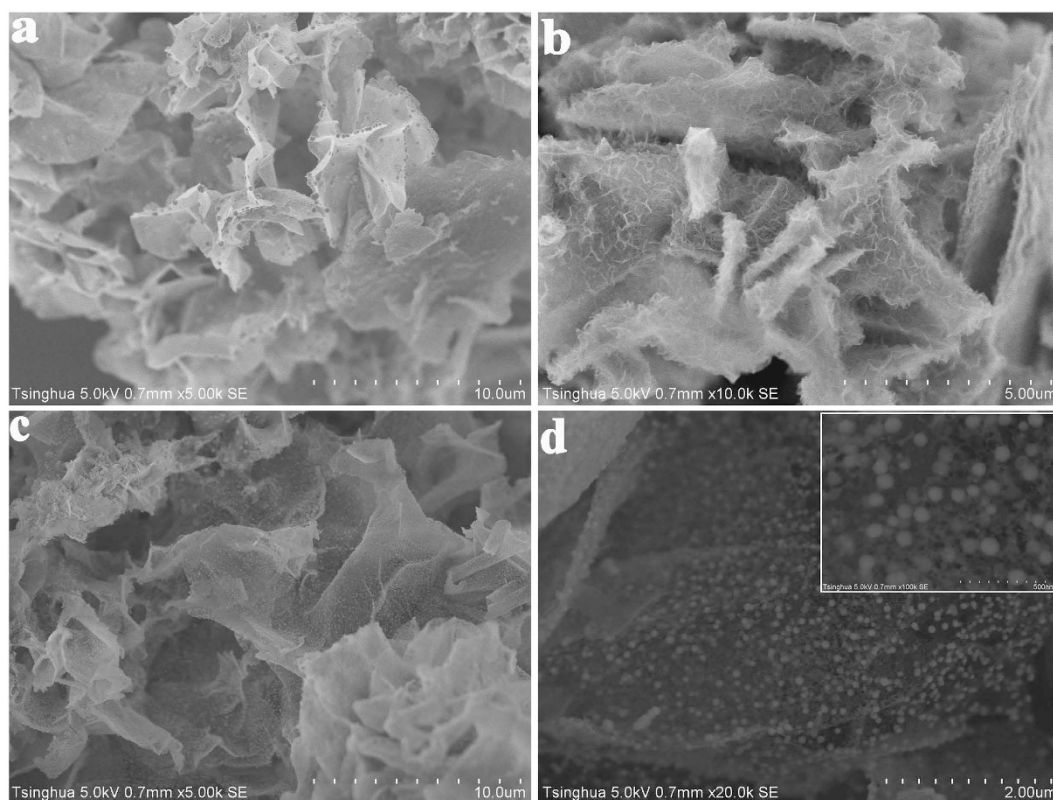
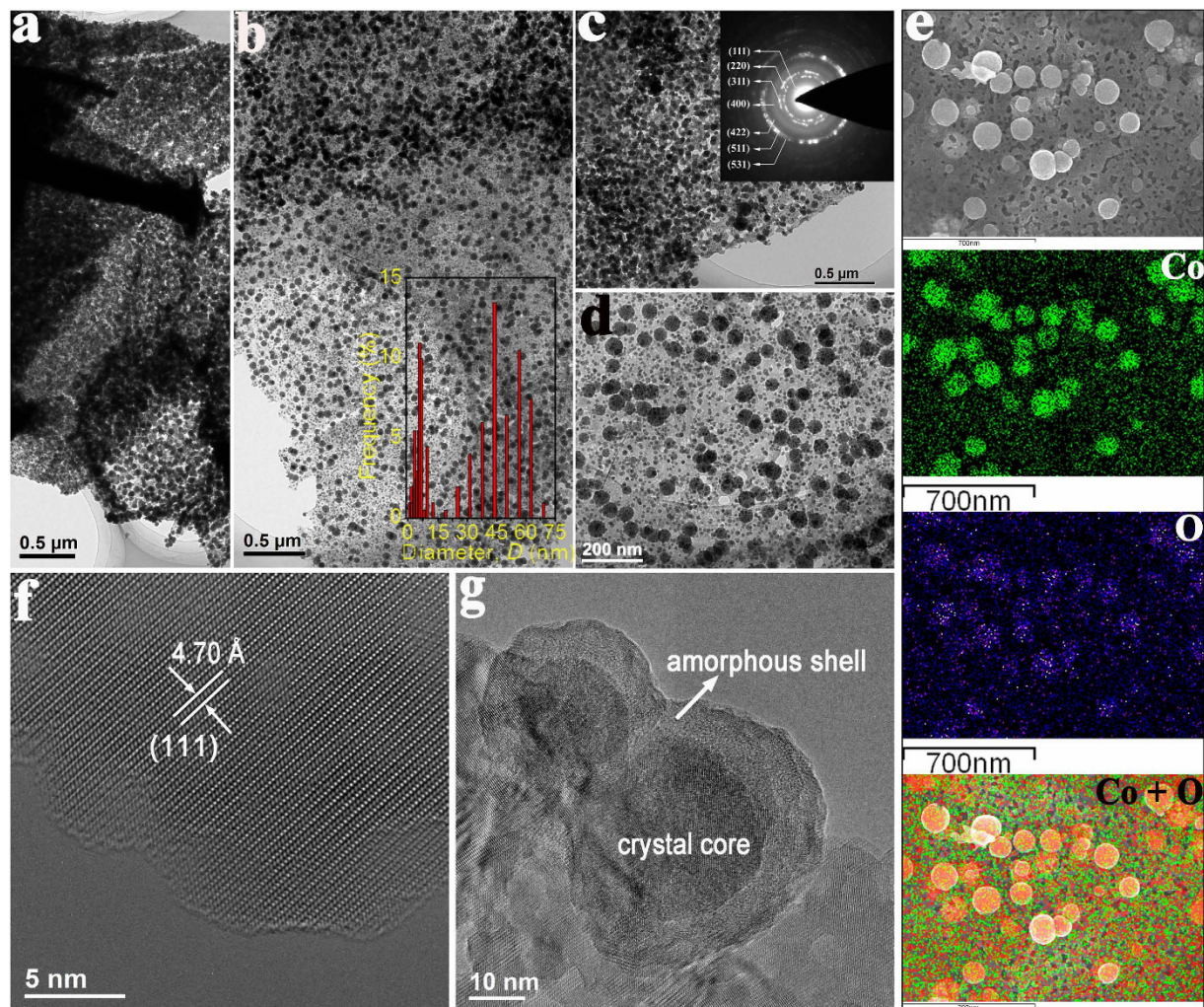


Figure 2. FESEM images of the Co<sub>3</sub>O<sub>4</sub> nanohybrids with different magnifications.



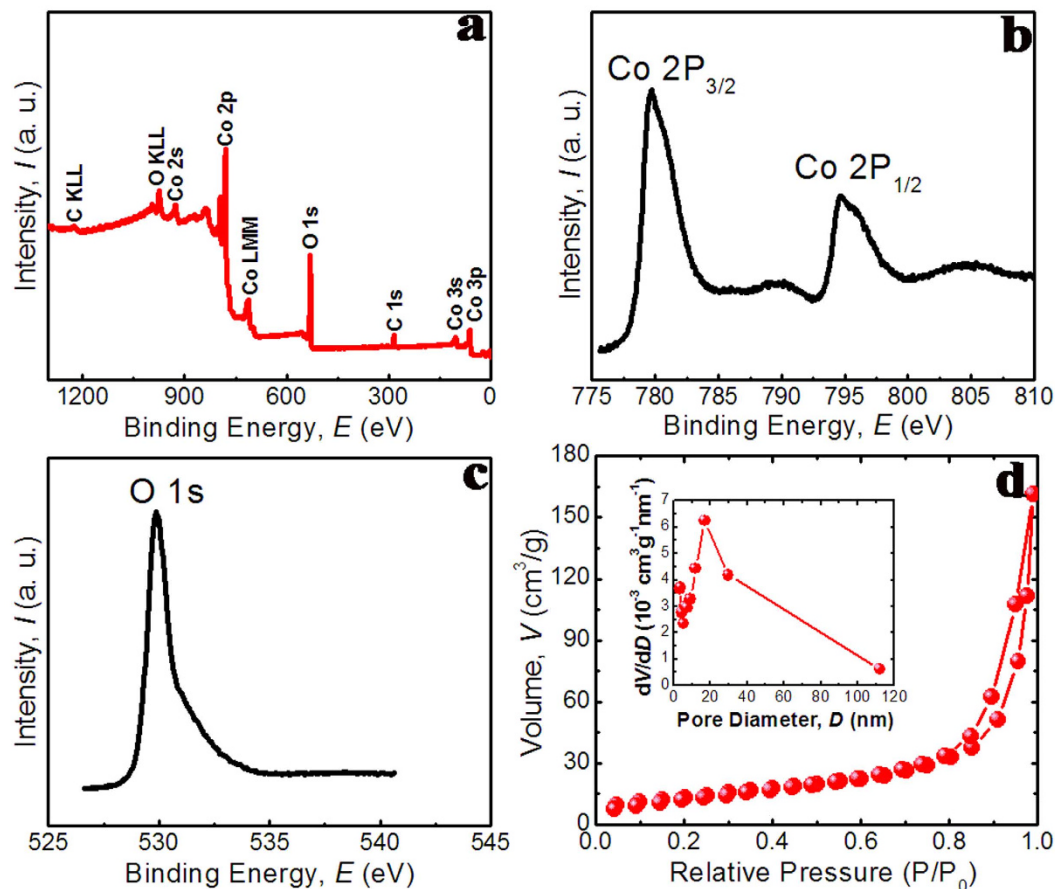
**Figure 3.** (a–d) TEM images of  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HNs, with the insets in (b,c) showing the size distribution profile of  $\text{Co}_3\text{O}_4$  nanoparticles and SAED pattern. (e) is SEM elemental mapping image showing the homogenous distribution of elements of Co and O in  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HNs. (f,g) are HRTEM images of nanosheet and core/shell nanoparticles, respectively.

core-amorphous shell structure. Additional HRTEM images for the nanoparticles are shown in Fig. S5, further demonstrating the crystalline@amorphous core/shell nature of  $\text{Co}_3\text{O}_4$  nanoparticles.

The surface chemical composition and oxidation state of  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HNs are determined by employing XPS analysis. The XPS spectrum of the HNs in the region of 0–1300 eV is shown in Fig. 4(a) and confirms the peaks of Co and O. The high resolution scan of Co 2p (Fig. 4b) exhibits two peaks located at 795.6 eV and 780.2 eV corresponding to the electronic states of Co  $2p_{1/2}$  and Co  $2p_{3/2}$  respectively. The presence of  $\text{Co}_3\text{O}_4$  can be further confirmed by the O 1s peak (Fig. 4c) located at 530.2 eV, which corresponds to the oxygen species forming oxide with cobalt elements.

Nitrogen adsorption–desorption isotherm is used to determine the specific surface area and the porous nature of the product. The  $\text{N}_2$  adsorption–desorption isotherm of  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HNs at 77K is presented in Fig. 4(d) with the inset displaying the corresponding Barret–Joyner–Halenda (BJH) pore size distribution. The isotherm shows a hysteresis loop at relative pressure range of 0.8–1.0  $P/P_0$  and the Bruauer–Emmett–Teller (BET) specific surface area is  $51.9 \text{ m}^2\text{g}^{-1}$ , which is higher than that of  $\text{Co}_3\text{O}_4$  nanosheets<sup>36</sup>. The higher surface area of  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HNs may be attributed to the mesoporous nature of the nanosheets and the void spaces between the nanoparticles. The BJH pore size distribution curves indicate that the average pore size is  $\sim 16 \text{ nm}$  for large pores and  $\sim 2 \text{ nm}$  for small pores (inset in Fig. 4d). The present porous  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HNs are of importance in lithium-storage process, due to their capability of providing extra active sites for the storage of lithium ions and facilitating mass diffusion and ion transport, which are induced by the synergistic reactions of porous structures and the specially designed structure of the constituent nanoparticles.

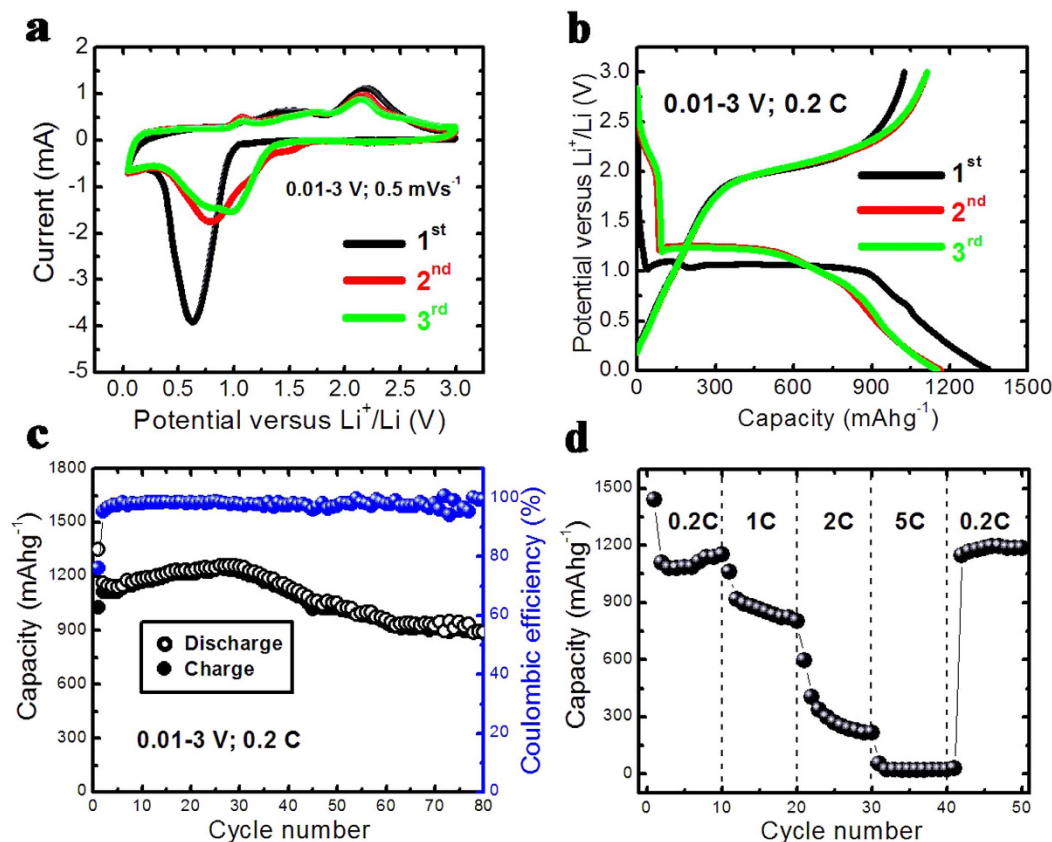
We subsequently study the electrochemical properties of  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HNs as an anode material for LIBs. Figure 5(a) displays the representative cyclic voltammograms (CVs) for the first three cycles at a scan rate of  $0.5 \text{ mV s}^{-1}$  in the voltage window between 0.01 and 3 V (versus  $\text{Li}^+/\text{Li}$ ). In the first cycle, there is a dominant



**Figure 4.** (a) XPS survey spectra of  $\text{Co}_3\text{O}_4$  nano hybrids, (b,c) high-resolution XPS spectra of the Co 2p and O 1s regions, respectively, (d) Nitrogen adsorption–desorption isotherms and corresponding pore size distribution curve (inset) of the  $\text{Co}_3\text{O}_4$  nano hybrids.

cathodic peak at  $\sim 0.62$  V which can be ascribed to the electrochemical reduction (lithiation) reaction of  $\text{Co}_3\text{O}_4$  with Li. In the following anodic scan the anodic peak at  $\sim 2.2$  V is ascribed to the oxidation (delithiation) reaction of  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HN. In the second cycle, the main reduction and oxidation peaks are shifted to  $\sim 0.78$  V and  $\sim 2.16$  V respectively, and the intensity of reduction peaks decreases due to the formation of irreversible solid electrolyte interface (SEI) film and the irreversible reduction reaction<sup>40,41</sup>. The peaks intensity and the integral areas of the third cycle are very close to that of the second cycle. These results show a gradual improvement in the electrochemical reversibility of  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HN after the first cycle.

Figure 5b shows the representative galvanostatic charge–discharge voltage profiles of  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HN at a current density of 0.2 C (1 C =  $890 \text{ mAhg}^{-1}$ ) in the voltage window of 0.01–3 V (versus  $\text{Li}^+/\text{Li}$ ) at room temperature. Similar to the previous report<sup>40,41</sup>, in the first discharge curve, the potential value quickly falls to the plateau ( $\sim 1.00$  V), and the extended plateau with a  $\sim 900$  mAh/g capacity may likely be ascribed to the conversion from  $\text{Co}_3\text{O}_4$  to Co, and then gradually declines to the cutoff voltage (0.01 V), which could be associated with the formation of a polymer/gel-like film on the surface of  $\text{Co}_3\text{O}_4$  particles<sup>40,41</sup>. The electrode delivers first-cycle discharge and charge capacities of 1349.4 and  $1025.6 \text{ mAhg}^{-1}$ , respectively, yielding an irreversible capacity loss of 24%. Such initial irreversible capacity loss mainly originates from the formation of SEI layer due to the irreversible degradation of the electrolyte and other irreversible side reactions<sup>22–26,35,40</sup>. The following two (2<sup>nd</sup> and 3<sup>rd</sup>) discharge/charge curves tend to be stable and exhibit similar electrochemical behavior. The discharge and charge capacities are 1165.3 and  $1111.8 \text{ mAhg}^{-1}$  for the second cycle, and 1150.2 and  $1112.2 \text{ mAhg}^{-1}$  for the third cycle, corresponding to the Coulombic efficiency of 95.4% and 96.7%, respectively. We notice that all of the capacities as mentioned above are higher than the theoretical total capacity of  $\text{Co}_3\text{O}_4$  ( $890 \text{ mAhg}^{-1}$ ), which is probably caused by the reversible formation/dissolution of the polymer/gel-like film contributing to an additional reversible capacity besides the electrochemical conversion reaction between cobalt oxide and  $\text{Co}^{40,41}$ . Figure 5(c) shows the discharge–charge cycling performance of  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HN evaluated between 0.01 and 3 V (versus  $\text{Li}^+/\text{Li}$ ) at a current density of 0.2 C at room temperature. It is found that the capacities of the following cycles from the fourth cycle increase slowly and gradually. The maximum discharge capacities could reach up to  $1262 \text{ mAhg}^{-1}$ . The possible reason is that the diffusion of Li-ion is activated and stabilized gradually during cycling process<sup>42</sup>. The capacities then fall slowly and nearly keep constant after 80 cycles. A reversible capacity of  $888.8 \text{ mAhg}^{-1}$  can be retained after 80 cycles.



**Figure 5.** Electrochemical measurements of  $\text{Co}_3\text{O}_4$  nanohybrids: (a) CVs at a scan rate of  $0.5 \text{ mV s}^{-1}$  between 0.01 and 3 V, (b) galvanostatic charge/discharge voltage profiles for the 1st, 2nd, and 3rd cycles between 0.01 and 3 V versus  $\text{Li}/\text{Li}^+$  at a current density of 0.2 C, (c) cycling performance at a constant current rate of 0.2 C between 0.01 and 3 V and (d) rate capability at various current rates between 0.2 C and 5 C.

To further evaluate the rate capability, the  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HN electrode is cycled at various current densities between 0.2 C and 5 C as shown in Fig. 5(d). The charge/discharge rates are programmably modified from 0.2 C to 1 C, 2 C, 5 C and then back to 0.2 C for 10 cycles. It can be found that the discharge and charge capacities remain stable and decrease regularly with an increased current rate. After every 10 cycles at a specific current rate, the reversible capacity at 0.2, 1, 2, and 5 C are about 1151.9, 804, 216.9 and 22.2  $\text{mAhg}^{-1}$ , respectively. When the current density is decreased from 5 to 1 C, the reversible capacity can be recovered to 1186.3  $\text{mAhg}^{-1}$ . These results demonstrate that the  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HN electrode has good electrochemical reversibility.

## Discussion

The lithium-storage properties, including the capacity, cycling performance especially the rate capacity of the  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HN electrode are superior to that of most nanostructured  $\text{Co}_3\text{O}_4$  materials, such as porous  $\text{Co}_3\text{O}_4$  NWs arrays,  $\text{Co}_3\text{O}_4$  nanowires, flower-like porous  $\text{Co}_3\text{O}_4$  spheres, porous  $\text{Co}_3\text{O}_4$  needles, and so on (see Table S1). The good lithium storage properties of  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HN might be attributed to the rationally designed hierarchical nanostructures. Firstly, the porous nanosheets and the amorphous shell of the  $\text{Co}_3\text{O}_4$  nanoparticles can accommodate the local volume change upon charge/discharge cycling and is likely to alleviate the problem of pulverization and aggregation of the electrode material, thus leading to improved cycling stability<sup>43–47</sup>. Furthermore, the hierarchical architecture assembled with 0D nanoparticles and 2D nanosheets is favorable for preventing the aggregation of the constituted nanobuilding blocks, also improving the cycling performance<sup>35,48</sup>. Secondly, the hierarchical structures with high density  $\text{Co}_3\text{O}_4$  decorated nanosheets provide sufficient electrode-electrolyte contact area for the storage of lithium ions, which is beneficial for enhancing the specific capacity. Moreover, the amorphous shell could offer additional reaction sites on the surface, which is also responsible for the high specific capacity of the  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HN electrodes<sup>43,45,47</sup>. Finally, the crystalline  $\text{Co}_3\text{O}_4$  cores and nanosheets have the functions of providing stable mechanical support and an efficient electrical conducting pathway, while the amorphous  $\text{Co}_3\text{O}_4$  shells could give reliable continuous pathways for  $\text{Li}^+$  during the course of continuous charge/discharge processes, enhancing the kinetics and structural stability for lithium storage<sup>47</sup>. As a result of the above-mentioned advantages, the prepared  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HN electrode expectedly manifests enhanced lithium storage properties.

In conclusion, we report the synthesis of unique  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HN, in which crystalline@amorphous core/shell  $\text{Co}_3\text{O}_4$  nanoparticles with a bimodal size distribution uniformly disperse on ultrathin  $\text{Co}_3\text{O}_4$

nanosheets. When used as the anode materials of LIBs, the as-prepared  $\text{Co}_3\text{O}_4$  C@A NPs-NSs HNs electrodes delivered high lithium storage properties, including a high reversible capacity of  $1053.1 \text{ mAhg}^{-1}$  after 50 cycles at a current density of  $0.2 \text{ C}$ , good cycling stability and rate capability. It is believed that the excellent electrochemical performance can be attributed to the uniquely designed hierarchical nanostructures. The present facile synthesis route can be applied to other metal oxides with desirable nanostructures and functions.

## Methods

**Materials Synthesis.** All of the reagents are analytical grade and used as received. Firstly,  $1.45 \text{ g}$  of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $1.4 \text{ g}$  of HMT (hexamethylenetetramine,  $\text{C}_6\text{H}_{12}\text{N}_4$ ) were dissolved in  $30 \text{ ml}$  of water under stirring for  $30 \text{ min}$ . The mixture was then transferred into a Teflon-lined stainless steel autoclave ( $50 \text{ ml}$  capacity). The autoclave was sealed and maintained at  $95^\circ\text{C}$  for  $8 \text{ h}$ . After cooling down to room temperature spontaneously, the precipitate is rinsed with distilled water and ethanol, and dried at  $60^\circ\text{C}$  under vacuum for  $2 \text{ h}$ . Finally, the product was annealed at  $450^\circ\text{C}$  in air for  $2 \text{ h}$ . The annealed samples were then soaked in  $1 \text{ M NaBH}_4$  solution ( $20 \text{ ml}$  distilled water). The sample was collected after an hour and washed with distilled water three times. Finally, the product was collected after centrifugation and dried in an oven at  $70^\circ\text{C}$  for  $10 \text{ h}$ .

**Characterization of Materials.** The phases of the unreduced and reduced products were characterized by X-ray diffraction (XRD). The morphology and structure of the products were obtained by field emission scanning electron microscopy (FESEM, Hitachi S5500), transmission electron microscopy (TEM, FEI Tecnai G<sup>2</sup> 20,  $200 \text{ kV}$ ), high resolution transmission electron microscopy (HRTEM, FEI Titan 80–300,  $300 \text{ kV}$ ), and X-ray photoelectron spectroscopy (XPS, Escalab 250, Al  $\text{K}\alpha$ ). The elemental mapping was done by using energy dispersive X-ray spectroscopy (EDS). The surface area of the products was measured by the Bruauer–Emmett–Teller (BET) method using nitrogen adsorption–desorption isotherm. Pore size distribution plots were obtained by the Barret–Joyner–Halenda (BJH) method. Thermogravimetric (TG) analysis was carried out on a TGA 2050 thermogravimetric analyzer under an air atmosphere at the temperature range of  $25\text{--}500^\circ\text{C}$  with a heating rate of  $10^\circ\text{C min}^{-1}$ .

**Electrochemical Measurements.** To measure the electrochemical performance, the electrodes were constructed by mixing the active materials, conductive carbon black and carboxymethyl cellulose, in a weight ratio of  $80:10:10$ . The mixture was prepared as slurry and spread onto copper foil. The electrode was dried under vacuum at  $120^\circ\text{C}$  for  $5 \text{ h}$  to remove the solvent before pressing. Then the electrodes were cut into disks ( $12 \text{ mm}$  in diameter) and dried at  $100^\circ\text{C}$  for  $24 \text{ h}$  in vacuum. The cells were assembled inside an Ar-filled glove box by using a lithium metal foil as the counter electrode and the reference electrode and microporous polypropylene as the separator. The electrolyte used was  $1 \text{ M LiPF}_6$  dissolved in a mixture of ethylene carbonate (EC), propylene carbonate (PC), and diethyl carbonate (DEC) with a volume ratio of  $\text{EC/PC/DEC} = 3:1:1$ . The assembled cells were allowed to soak overnight, and then the electrochemical tests on a LAND battery testing unit were performed. Galvanostatic charging and discharging of the assembled cells were performed at different current rates between voltage limits of  $0.01$  and  $3 \text{ V}$  (vs.  $\text{Li}^+/\text{Li}$ ) at room temperature. The cyclic voltammogram (CV) was performed at a scan rate of  $0.5 \text{ mVs}^{-1}$  in the range of  $0.01\text{--}3.00 \text{ V}$  (vs.  $\text{Li}^+/\text{Li}$ ).

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## Author Contributions

J.M. and H.S. conducted the main experiments. G.H., K.M., Y.L., Y.Z., X.W. and S. X. assisted in the synthesis and specimen treatment. H.S. and J.Z. conceived and designed the work and were responsible for the work. All authors discussed the results, wrote and commented on the manuscript.

## Additional Information

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