# Hierarchical Co@C Nanoflowers: Synthesis and Electrochemical Properties as an Advanced Negative Material for Alkaline Secondary Batteries

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# **Supporting Information**

**ABSTRACT:** Hierarchical Co@C nanoflowers have been facilely synthesized via a simple route based on a low-temperature solid-phase reaction. The obtained hierarchical Co@C nanoflowers, each constructed of a number of nanosheets, display a three-dimensional architecture with an average grain size of about 300 nm. The electrochemical properties of the Co@C nanoflowers as the negative material for Ni/Co cells have been systemically researched. In particular, Co@C material exhibits high discharge-specific capacity and good cycling stability. The discharge-specific capacity of our Co@C-3 electrode can reach 612.1 mA h g<sup>-1</sup>, and the specific capacity of 415.3 mA h g<sup>-1</sup> is retained at a current density of 500 mA g<sup>-1</sup> after 120 cycles, indicating its great potential for high-performance Ni/Co batteries. Interestingly, the as-synthesized Co@C electrode also exhibits favorable rate capability. These desirable properties can be attributed to porous pathways, which allow fast transportation of ions and electrons and easy accessibility to the electrolyte. The dominant electrochemical



mechanism of Co@C can be attributed to the reduction-oxidation reaction between metallic cobalt and cobalt hydroxide in alkaline solution.

KEYWORDS: Co@C, nanoflowers, low-temperature solid-phase reaction, electrochemical properties, alkaline secondary battery

# 1. INTRODUCTION

As an important energy storage system, alkaline rechargeable Ni/Co batteries have been attracting considerable attention owing to its high power and energy densities, low price, and reversible electrochemical redox reactions.<sup>1–3</sup> According to Gao et al.,<sup>3</sup> the Ni/Co cell exhibits a higher specific energy (about 160 Wh kg<sup>-1</sup>) than commercial nickel metal hydride (Ni/MH) batteries (70–90 Wh kg<sup>-1</sup>). What is more, the Ni/Co cells also exhibit good cycling stability and high rate capability.

In recent decades, Co-based materials have been extensively explored and comprehensively studied due to their excellent electronic, magnetic, catalytic, gas sensing, and photoelectrochemical performances.<sup>4–11</sup> Their potential applications in energy storage devices are attracting more and more attention, however, due to the extensive development of sustainable energy with less pollution, and the anode of Ni/Co alkaline rechargeable batteries has been a particular focus of attention. The advantages of these Co-based negative materials for Ni/Co cells can be thusly described: outstanding cycling stability, high rate capability, good electrical conductivity, and specific capability for multi-electron reactions in charge and discharge processes.

Nanostructure engineering has been considered as a powerful and effective route by which to design novel electrode materials with outstanding electrochemical properties through both morphological and compositional solutions.<sup>12–15</sup> Recently, a variety of Co nanomaterials with controlled morphologies, such as nanowires, nanodisks, nanotubes, and polyhedral and chainlike structures, have been found to significantly enhance the electrochemical properties of Ni/Co cells.<sup>16–18</sup> The active substance of these Co-based materials during charge and discharge has been proved to be metallic Co. Therefore, the utilization of metallic cobalt is one of the most key factors that influence the electrochemical properties of Co-based materials, which is mainly dependent on the contact area between alkaline aqueous electrolyte and the active electrode material.<sup>19–21</sup>

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Moreover, grain size may determine the rate capability and electrical conductivity of a Ni/Co battery.<sup>18</sup> Therefore, the morphology structure and particle size of materials will affect the electrical conductivity of the electrode, ultimately influencing the discharge-rate capability and specific capacity of the batteries. Therefore, it is urgent to synthesize a metallic Co material with unique morphology and a large specific surface area to improve the electrochemical properties of Co-based negative materials.

In our previous study, we found that the introduction of CMK-3 was an effective strategy for enhancing the electrochemical properties of metallic Co.<sup>21</sup> In addition, there were also some reports in the literature<sup>21-27</sup> that nonmetallic materials, such as sulfur, carbon, silicon, and BN, could also enhance the electrochemical performances of metallic cobalt because the nonmetallic materials increased the contact area between the alkaline aqueous electrolyte and the active electrode material. They also can increase the dispersion of the active electrode material. On the basis of the above considerations, hierarchical Co@C nanoflowers composites were synthesized via a simple method, based on a lowtemperature solid-phase reaction, using benzimidazole as the reductant and carbon precursor. More importantly, the template-free synthesis of the nanoflower structure is facile. As-synthesized hierarchical Co@C nanoflowers constructed of a number of nanosheets display a three-dimensional architecture with an average nanoflower size of about 300 nm. The obtained Co@C samples show high discharge-specific capacity, good rate capability, and good cycling stability when evaluated as anode material in Ni/Co alkaline rechargeable batteries. The specific capacities can reach 611.2 (1st cycle) and 415.3 mAh  $g^{-1}$  (120th cycle) at 500 mA  $g^{-1}$ .

# 2. EXPERIMENTAL SECTION

**2.1. Preparation of Hierarchical Co@C Nanoflowers.** Hierarchical Co@C nanoflowers were synthesized via a green and effective method via a low-temperature solid-phase reaction. In a typical synthesis of Co@C material, the weight ratios of LiOH·H<sub>2</sub>O, benzimidazole, and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were 3:1:2, 3:1:3, and 3:1:4, respectively. These precursors were ground together in a carnelian mortar for 30 min. Next, the mixture was heated with a heating ramp of 5 °C min<sup>-1</sup> and maintained at 400 °C for 4 h in Ar. After being washed several times with deionized water and absolute ethyl alcohol, the wet products were dried at 60 °C for 12 h in a vacuum. The corresponding samples prepared from the different weight ratios of 3:1:2, 3:1:3, and 3:1:4 were marked as Co@C-2, Co@C-3, and Co@ C-4, respectively.

**2.2. Structural Characterization.** The as-synthesized Co@C materials were measured by X-ray diffraction (XRD, Rigaku D/Max-2500, filtered Cu K $\alpha$  radiation,  $\lambda = 0.1542$  nm) and Raman spectroscopy (Renishaw inVia). The morphologies of these materials were observed using scanning electron microscopy (SEM, JEOL JSM-6700F), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100 TEM). Nitrogen adsorption and desorption measurement was also conducted on a NOVA 2000e (Quantachrome Instruments) to determine the specific surface area. The amounts of carbon of Co@C materials were determined by elemental analysis (vario EL cube). The as-synthesized Co@C materials were characterized by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe, ULVAC PHI).

**2.3. Electrochemical Characterization.** The as-synthesized Co@ C materials were constructed through a new smear method. The asprepared Co@C materials, carbonyl nickel powders, and polytetra-fluoroethylene (PTFE) were ground in a weight ratio of 25:70:5 and coated on Ni foam. The cells were assembled in a three-compartment cell using Hg/HgO as the reference electrode, NiOOH/Ni(OH)<sub>2</sub> as

the counter electrode, and KOH aqueous solution (6 M) as the electrolyte. Electrochemical measurements were conducted using a LAND CT2001 battery testing system (Wuhan LAND Electronics). The as-prepared electrodes were charged at 200 mA g<sup>-1</sup> for 4 h and discharged at different current densities with the cutoff voltage at -0.5 V (vs Hg/HgO). There was a 5 min interval between the charge and discharge processes.

# 3. RESULTS AND DISCUSSION

**3.1. Synthesis and Characterization.** Hierarchical Co@C nanoflowers were synthesized via a green and effective method based on a low-temperature solid-phase reaction using benzimidazole as the reductant and carbon precursor. Typical XRD patterns of hierarchical Co@C nanoflowers are displayed in Figure 1a. The XRD patterns of all of the samples are



Figure 1. XRD patterns (a) and Raman spectra (b) of the assynthesized hierarchical Co@C samples.

consistent with each other, and they agree well with the cubic Co (JCPDS: 15–806) phase. The cell parameters of Co@C-2, Co@C-3, and Co@C-4 can be determined to be a = 3.546, 3.540, and 3.542 Å, respectively, which are very close to the 3.5447 Å given in JCPDS card no. 15-806 for the cubic Co phase. No peaks from impurity phases can be detected, demonstrating high purity of hierarchical Co@C nanoflowers. The amounts carbon of the as-synthesized Co@C-2, Co@C-3, and Co@C-4 samples are 25.29, 14.63, and 9.30 wt %, respectively. Obviously, the carbon content decreases with increasing ratio of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.

Raman spectra of the hierarchical Co@C nanoflowers are presented in Figure 1b. The Raman spectra (Figure 1b) of all three samples contain two peaks at about 1355 and 1583 cm<sup>-1</sup> that correspond to the D and G bands of carbon, respectively. The D band can be assigned to typical disorder, while the G band is characteristic of graphene. The intensity ratio between the D and G bands ( $I_D/I_G$ ) provides information on the density of defects that prevails in the sample. The  $I_D/I_G$  values for the Co@C-2, Co@C-3, and Co@C-4 samples are around 1.1, 1.0, and 0.58, respectively, which are higher than the  $I_D/I_G$  value (0.09) of fully graphitized carbon.<sup>28–31</sup> This demonstrates that the carbon in the hierarchical Co@C material is amorphous,

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that the degree of graphitization of carbon has decreased, and the defects have increased in Co@C. The above results also prove that as-obtained composites have a large amount of void space for volume expansion and provide numerous electroactive sites for redox reactions. In addition, carbon can facilitate electron transfer by improving the electrical conductivity, and hence, it is conducive to enhanced electrochemical properties.<sup>32,33</sup>

It was found that the morphology and structure of a Co@C sample can also be dramatically affected by the ratio of reactants. The morphologies of Co@C samples with different ratios of reactants were analyzed by SEM. As shown in Figure S1a, the Co@C-2 sample is entirely composed of nanoplate structures. When the ratio of reactants is 3:1:3, the Co@C-3 product displays hierarchical nanoflower structures assembled from a number of nanosheets (Figure S1b). More importantly, the template-free synthesis of the nanoflower structure is facile. When we continue to increase the amount of  $Co(NO_3)_2 \cdot 6H_2O$ (Co@C-4 sample), the hierarchical nanoflowers become aggregated (Figure S1c, Supporting Information). The above results indicate that the ratio of reactants is important for the formation of the hierarchical nanoflower structure. As shown in Figure S2, carbon content of Co@C-3 is 13.58 wt %, which agrees with the results obtained by EA, demonstrating that the main component of hierarchical Co@C nanoflower is metallic Co.

Figure 2 shows typical SEM and TEM images of hierarchical Co@C-3 nanoflowers. It can be seen that the Co@C-3  $\odot$ 



Figure 2. SEM (a) and TEM (b,c) images, HAADF STEM micrographs (d), and element mapping images (e,f) of as-synthesized hierarchical Co@C samples.

nanoflowers with an average grain size of about 300 nm are assembled from a number of sheet-like subunits (Figure 2a). The TEM images in Figure 2b further prove that Co@C-3 material has a nanoflowerlike morphology composed of nanosheets. The inset of Figure 2b shows that the nanosheets are thin,  $\sim 2-3$  nm, as highlighted by the arrows, and gather in a ring in the center. The HRTEM image in Figure 2c reveals a fringe spacing of around 0.203 nm, corresponding to the (111) plane of cubic Co. Therefore, we believe that the hierarchical nanoflower structure and ultrathin nanosheets can increase the contact area between the alkaline aqueous electrolyte and active electrode material. This may be more beneficial for reducing transport paths and offering robust retention of electrolyte ions. To further analyze the carbon distribution in the Co@C-3 sample, we used scanning TEM. (Figure 2d-f). The region analyzed using EDX elemental mapping is indicated by the square in Figure 2d. The elemental mapping images in Figure 2e,f demonstrate that the carbon distribution in the Co@C-3 sample is quite uniform and completely without any detectable aggregation. We believe that the in situ process is beneficial for high interfacial interaction between the Co and C in the Co@C-3 sample. Thus, the intimate combination of Co with electronically conducting carbon allows for rapid and efficient charge transport, which can lead to great improvement of electrochemical properties.

To further evaluate near-surface elemental composition and chemical states in the as-obtained Co@C-3 nanoflowers, we conducted XPS. The spectra of as-obtained Co@C-3 nanoflowers are presented in Figure 3. The peak (Figure 3a) located



Figure 3. XPS spectra of Co 2p (a) and C 1s (b) for as-synthesized hierarchical Co@C nanoflowers.

at 778.5 eV is assigned to the characteristic peak of Co  $2p_{3/2}$ , suggesting the presence of zero valence Co. In addition, the peak (Figure 3b) centered at 284.6 eV is referred to characteristic peak of C 1s. The presence of zero valence Co and C confirms the successful deposition of Co@C material.

Nitrogen adsorption and desorption measurements of the assynthesized Co@C-3 nanoflowers were further performed to obtain more information on the porous structure (Figure S3a,b). The type IV isotherms can be assigned to type of H3 hysteresis loops, indicating the presence of mesoporous structure.<sup>22,34</sup> The BET value of Co@C-3 nanoflower sample is about 31.6 m<sup>2</sup> g<sup>-1</sup>. Figure S3b shows the pore-size distribution calculated by the Barrett–Joyner–Halenda (BJH) method. It shows an average pore-size value of about 3.81 nm. We believe that the mesoporous structure is critical for facilitating the transfer of electrons and ions in the interface between the electrode and electrolyte and offers many active sites for fast electrochemical reactions. This may lead to a great enhancement of electrochemical properties.

**3.2. Electrochemical Properties.** The electrochemical properties of the hierarchical Co@C nanoflowers were

evaluated under different current densities. Long-term cycling performance is well-known as a key parameter for Ni/Co battery applications. Figure 4 exhibits the cycle life of the Co@



Figure 4. Cycle life of the as-synthesized hierarchical Co@C nanoflowers at 300 mA  $\rm g^{-1}.$ 

C electrodes in 6 M KOH solution at 300 mA g<sup>-1</sup>. Obviously, the Co@C-3 electrode exhibits excellent discharge-specific capacity and cycling stability, and the discharge-specific capacity can reach around 608.7 mAh  $g^{-1}$ . We can see that about 65.7% of the specific capacity can be retained after 120 cycles (399.7 mAh  $g^{-1}$ ), suggesting the good long-term electrochemical stability of the Co@C-3 nanoflowers. This may be due to the unique hierarchical structure of Co@C-3 nanoflowers, which improves electrical conductivity and enlarges the contact area between the alkaline electrolyte solution and the active electrode material, further promoting the utilization of Co as the active electrode material. In addition, the nanoflowers are assembled from a number of ultrathin nanosheets, which provide numerous electroactive sites for redox reactions. The Co@C-2 and Co@C-4 electrodes show inferior cycling stability and discharge capacity, however, possibly resulting from their compact particles and the agglomeration of their hierarchical nanoflowers, which go against electrochemical reaction. Furthermore, too high a content of carbon (Co@C-4 electrode) is also not beneficial for improving the electrochemical properties, owing to the decreased active-material density in the electrode. We thus conclude that moderate carbon content can further improve the utilization of Co. Therefore, the hierarchical Co@C-3 composite facilitates electron transfer, leading to the improvment of discharge specific capacity and cycling stability.

To examine the kinetic properties of the as-snythesized Co@ C-3 electrode, we measured the rate capabilities at various current densities (Figure 5a). The delivered discharge specific capacities are 608.7, 612.1, and 542.2 mA h g<sup>-1</sup> at 300, 500, and 1000 mA  $g^{-1}$ , respectively. It decreases to 399.7, 415.3, and 260.8 mAh  $g^{-1}$  at the 120th cycle, respectively. In addition, specific capacities (Figure 5b) of Co@C-3 are 611.2, 494.7, 461.6, 449.2, and 446.1 mAh  $g^{-1}$  at 100, 200, 300, 500, and 1000 mA  $g^{-1}$ , respectively. The above results suggest good rate capability of as-synthesized Co@C-3 materials. It is worth noting that the discharge-specific capacities of Co@C-3 are much higher than those of AB<sub>3</sub> alloy, exhibiting its potential application as an alternative negative material for Ni/Co batteries.<sup>25</sup> This stable performance may be attributed to the advantageous structural features of the Co@C-3 material. The hierarchical nanoflowers are constructed from a number of ultrathin nanosheets, which facilitates the effective exposure of active sites. These more numerous active sites provide more reaction sites that benefit from better electrolyte penetration



**Figure 5.** (a) Cycle life at different discharge-current densities and (b) rate capability of as-synthesized hierarchical Co@C nanoflowers.

and charge transfer, leading to improved electrochemical performance.

Figure 6 presents charge and discharge curves of assynthesized Co@C-3 electrode at 500 mA  $g^{-1}$ . The initial



Figure 6. Charge and discharge curves of the as-synthesized hierarchical Co@C nanoflowers.

discharge specific capacity of Co@C-3 electrode is 612.1 mAh  $g^{-1}$ , and it then reduces to 505.2 mAh  $g^{-1}$  at the 50th cycle. Obviously, there is one potential plateau and two potential plateaus in the discharge and charge curves, respectively. The discharge potential plateaus for different cycles appear at about -0.78 V. The first charge-voltage plateau appears at about -0.88 V, and the other on located at about -1.03 V is attributed to the electrolysis of water. The above results coincide with the other Co-based negative electrode in Ni/Co batteries.<sup>12,19-25</sup>

The superior electrochemical performance of the hierarchical Co@C nanoflowers was further confirmed by the CV measurements. Figure 7 presents the CV curves of assynthesized Co@C-3 electrode for the initial few cycles. A pair of remarkable reduction and oxidation peaks appears in the CV curves. Cathodic peaks can be found at -0.98 V, and anodic peaks appear at about -0.71 V. In addition, the peak voltage and shape of CV curves for the as-synthesized Co@C-3 electrode are very similar to those for other Co-based negative electrodes, implying that the same electrochemical reactions



Figure 7. CV curves of as-synthesized hierarchical Co@C nanoflowers.

occur on the Co@C-3 electrode.<sup>24,35</sup> Therefore, the specific capacity of as-synthesized Co@C-3 electrode is mainly attributable to the metallic Co. As shown in Figure 7, the discharge-specific capacity gradually decreases with the reduction of the integral area of the CV curves during cycling. Taken together, these results are consistent with our previous conclusions on the cycling properties.

The XRD patterns of as-synthesized Co@C-3 in different charged and discharged states are shown in Figure 8. To avoid



Figure 8. XRD patterns of as-synthesized hierarchical Co@C nanoflowers in charged or discharged states after different cycles.

the influence of carbonyl Ni peaks, we used acetylene black as the conductive agent in the preparation of electrode for these XRD measurements. It is obvious that little metallic cobalt coexists with cobalt hydroxide in the first fully discharged state. Meanwhile, a small amount of cobalt hydroxide and metallic cobalt also appear in the first fully charged state. It suggests a partially irreversible transformation between metallic cobalt and cobalt hydroxide in charge and discharge processes, implying poor utilization of the hierarchical Co@C nanoflowers. In addition, the cobalt hydroxide intensity gradually increases in the second fully discharged state, demonstrating that the reduction and oxidation irreversibility of metallic cobalt increases gradually. Thus, we believe that the high dischargespecific capacity of the Co@C can be attributed to the reduction and oxidation reaction between metallic cobalt and cobalt hydroxide.  $^{3,5,7,12,25,36,37}$  We conclude that Co(OH)<sub>2</sub> is reduced to metallic cobalt and that metallic cobalt is oxidized to cobalt hydroxide during the charge and discharge processes, respectively. This can be expressed as follows:

$$\operatorname{Co} + 2\operatorname{OH}^{-} \xrightarrow{\operatorname{discharge}}_{\operatorname{charge}} \operatorname{Co(OH)}_{2} + 2e$$
 (1)

The above experimental results indicate that the high discharge-specific capacity, good rate capability, good cycling stability, and long-term cycling life of the as-synthesized hierarchical Co@C nanoflowers may be significantly influenced

by their high surface area, high electrical conductivity, and hierarchical nanoflower structure.

# 4. CONCLUSION

We have demonstrated a simple and template-free method for synthesizing hierarchical Co@C nanoflowers via a lowtemperature solid-phase reaction. The hierarchical Co@C nanoflowers exhibit excellent charge and discharge performance in the Ni/Co batteries, including high discharge-specific capacity (608.7 mA h g<sup>-1</sup>), good cycling stability (about 399.7 mA h g<sup>-1</sup> retained after 120 cycles), as well as good rate capability. SEM and TEM investigations reveal that Co@C-3, with hierarchical nanoflowers about 300 nm in size, is assembled from a number of sheet-like subunits. The porous structure of the as-prepared hierarchical Co@C nanoflowers could ensure more effective contact between alkaline aqueous electrolyte and electrode materials, resulting in enhanced electrochemical properties.

### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06603.

Figures showing SEM images of as-synthesized Co@C materials, the EDX pattern of the hierarchical Co@C nanoflowers, and N<sub>2</sub> adsorption and desorption isotherms of the hierarchical Co@C nanoflowers. (PDF)

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#### Notes

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