

Coordination Polymers Derived General Synthesis of Multishelled Mixed Metal-Oxide Particles for Hybrid Supercapacitors

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Metal–organic frameworks (MOFs) or coordination polymers (CPs) have been used as precursors for synthesis of materials. Unlike crystalline MOF, amorphous CP is nonspecific to metal cation species, therefore its composition can be tuned easily. Here, it is shown that amorphous CP can be used as general synthesis precursors of highly complex mixed metal oxide shells. As a proof of concept, Ni–Co coordination polymer spheres are first synthesized and subsequently transformed into seven-layered Ni–Co oxide onions by rapid thermal oxidation. This approach is very versatile and can be applied to produce ternary and quaternary metal oxide onions with tunable size and composition. The Ni–Co oxide onions exhibit exceptional charge storage capability in aqueous electrolyte with high specific capacitance ($\approx 1900 \text{ F g}^{-1}$ at 2 A g^{-1}), good rate capability, and ultrahigh cycling stability (93.6% retention over 20 000 cycles). A hybrid supercapacitor against graphene/multishelled mesoporous carbon sphere shows a high energy density of 52.6 Wh kg^{-1} at a power density of 1604 W kg^{-1} (based on active materials weight), as well as remarkable cycling stability.

Hollow metal oxide shells with controlled size, composition, and internal structure could be used in a wide range of applications, such as energy storage and conversion, catalysis, and drug delivery.^[1–12] Multishell structures can overcome a common drawback of simple hollow shell, namely, the low packing density originating from the large empty space inside. In addition, tunable composition/components may greatly improve the overall performance.^[13–15] For example, spinel nickel cobaltite (NiCo_2O_4) possesses much better electrical conductivity and higher electrochemical activity than Co_3O_4 or NiO .^[16,17] Until now, several types of multishelled metal oxides hollow particles have been successfully synthesized by

templating.^[7,18–20] For example, Wang and co-workers synthesized multishelled TiO_2 hollow microspheres using carbonaceous microspheres as hard templates, which exhibit higher lithium storage capacity and improved cycling performance compared with single-shelled TiO_2 microspheres.^[21] Lou et al. have reported a shell-by-shell templating method to fabricate double-shelled SnO_2 hollow spheres using silica spheres as hard template.^[22] Cu_2O hollow spheres with multishelled structures have also been prepared using a cationic surfactant, cetyltrimethylammonium bromide, as soft template.^[23] Previously we have reported a new “penetration–solidification–annealing” method to synthesize multishelled mixed metal oxide hollow spheres.^[24] Very recently, we have also developed a self-templating strategy to construct uniform NiCo_2O_4 hollow spheres with a core-double-shell

structure.^[25] Despite all these advances, the methods developed require tedious multistep synthesis. Also, the number of shells of the hollow particles obtained is generally less than four, limited by the amount of metal cations that can diffuse into the hard templates. Therefore, it is highly desirable to develop a general and efficient method for the synthesis of highly complex multishelled hollow particles with tunable composition.

Coordination polymers (CPs) or more commonly known as metal–organic frameworks (MOFs) are a novel class of materials constructed from metal ions and bridging organic linkers^[26–28] and have been proven to be promising precursors.^[29–34] For example, Prussian blue analogues $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ and $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$ nanocubes have been used to synthesize Co_3O_4 and Fe_2O_3 nanoboxes, respectively.^[35–37] CuO and $\text{CuO}/\text{Cu}_2\text{O}$ hollow polyhedra have been fabricated by using Cu-based HKUST-1 as the precursors.^[38,39] The multicomponent ball-in-ball hybrid metal oxides have also been fabricated by taking advantage of the ion exchange and thermal behavior of coordination polymer spheres (CPSs).^[40] Recently, porous spinel $\text{Zn}_x\text{Co}_{3-x}\text{O}_4$ hollow polyhedra have been reported by utilizing a novel heterobimetallic zeolitic imidazolate frameworks as the precursors.^[41] Despite the great progress that has been achieved, it is still challenging to generally derive ternary or quaternary metal oxide hollow structures with highly complex multishelled structures from very limited micro/nanosized

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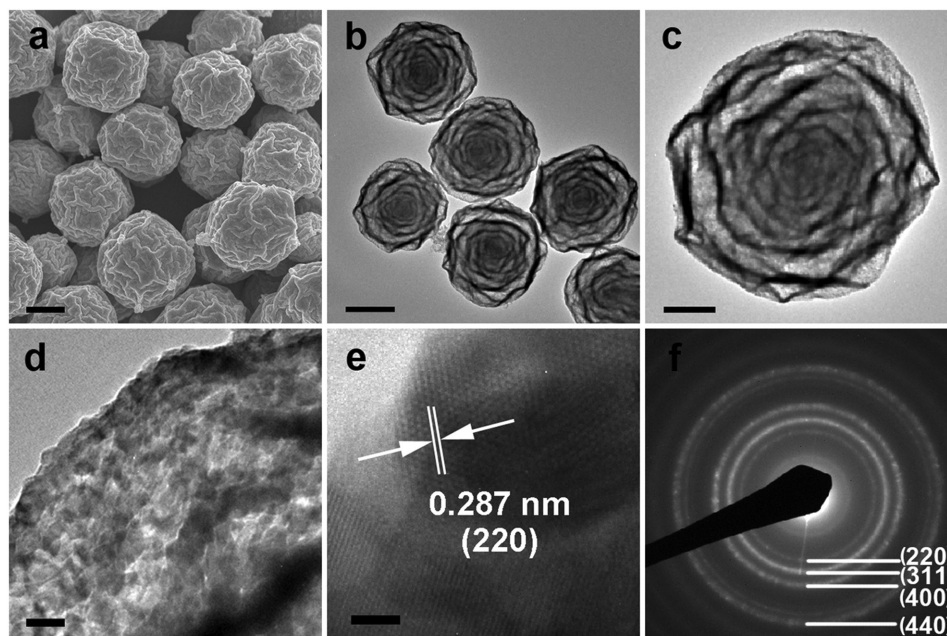


Figure 1. Microscopy characterizations of multishelled Ni–Co oxide particles. a) FESEM image (scale bar: 500 nm) and b) TEM image (scale bar: 500 nm). Magnified TEM images showing c) an individual multishelled Ni–Co oxide particle (scale bar: 200 nm) and d) the crystalline shell (scale bar: 20 nm). e) High-resolution TEM image of the Ni–Co oxide shell (scale bar: 2 nm) and f) the corresponding SAED pattern.

MOF or CP precursors. One great difficulty lies in the fact that most commonly known MOFs or CPs are crystalline and their formation is highly specific to certain metal cations.

Herein, we synthesize a unique class of amorphous CPSs as the precursor to generate multishelled mixed metal oxides. These amorphous CPSs are nonspecific to the metal cations incorporated, as the carboxylate ligands used have been widely demonstrated to be capable of forming coordinate bonds with most transition metal cations.^[42] Therefore, the composition of the derived multishelled particles can be easily controlled. To demonstrate the concept, Ni–Co CPSs are synthesized from coprecipitation of Co^{2+} and Ni^{2+} cations in the presence of organic ligand, isophthalic acid (H_2IPA). These Ni–Co CPSs can be easily oxidized in air, and the oxide layer formed is friable and spalls off on its own, to form seven-layered multishelled Ni–Co oxide particles without any other template. The synthesis approach in this study can be used as a universal route to synthesize multishelled particles of ternary and quaternary metal oxides with tunable size and composition, cheaply and with high yield. We demonstrate the versatility of this approach by synthesizing multishelled particles for many compositions and sizes. With both structural and compositional advantages, multishelled Ni–Co oxide particles manifest remarkable performance as electrode materials for electrochemical capacitors. Finally, liquid-cell in situ transmission electron microscopy observation is performed to investigate the charge/discharge behavior of Ni–Co oxide particles in alkaline electrolyte.

We first synthesize unique Ni–Co CPSs as the precursor from coprecipitation of Co^{2+} and Ni^{2+} cations in the presence of H_2IPA as the organic ligand via a solvothermal process. Field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images show that

these Ni–Co CPSs are uniform with an average size of about $1.2\ \mu\text{m}$ (Figure S1, Supporting Information). The powder X-ray diffraction (XRD) indicates the amorphous nature of Ni–Co CPSs (Figure S2, Supporting Information). Fourier transform infrared (FTIR) spectra verify that the band of C=O stretching vibration shifts from 1570 to $1510\ \text{cm}^{-1}$ after the formation of CP, demonstrating the coordination of carboxylate groups of H_2IPA to Co^{2+} and Ni^{2+} cations (Figure S3, Supporting Information). After the air thermal oxidation, the Ni–Co CP precursor is converted into Ni–Co oxide. The XRD pattern of the Ni–Co oxide sample is similar to the standard patterns of NiCo_2O_4 and Co_3O_4 (Figure S2, Supporting Information), revealing that the mixed Ni–Co oxide also adopts the spinel structure with similar lattice constants. As shown in Figure 1a, the as-synthesized Ni–Co oxide particles retain the spherical shape of their CP precursors. However, the diameter of Ni–Co oxide particles is reduced to about $1\ \mu\text{m}$, which is smaller than that of Ni–Co CPSs due to the shrinkage during calcination. Besides, the surface of the Ni–Co oxide particles becomes crumpled and rough, indicating the formation of thin shells consisting of small oxide nanograins. As revealed by TEM observation in Figure 1b, the as-synthesized Ni–Co oxide particles are composed of highly crumpled layers. Magnified image clearly demonstrates that the multishelled Ni–Co oxide particle possesses a unique seven-layered hollow structure (Figure 1c). Many connection parts between the crumpled neighboring layers can be seen throughout the whole structure, which may improve the structural stability of this material. Polycrystalline texture can be clearly observed within the thin layer of Ni–Co oxide nanoshell (Figure 1d). Consistent with the XRD analysis, a set of distinct lattice fringes with spacing of $0.287\ \text{nm}$ can be identified as the (220) planes of Ni–Co spinel oxide (Figure 1e). The distinct

selected area electron diffraction (SAED) pattern also confirms the spinel phase of the sample (Figure 1f). Energy-dispersive X-ray spectroscopy (EDX) analysis shows the Ni/Co molar ratio is about 1:1 within the final multishelled Ni–Co oxide particles (Figure S4, Supporting Information), which is in accordance to the relative amount of metal nitrate reactants used for preparation of CP precursors. The chemical composition of the sample is further measured using inductively coupled plasma optical emission spectroscopy (ICP-OES). The Ni/Co molar ratio for the multishelled Ni–Co oxide particles determined by the ICP-OES analysis is about 1:1.09, which is very close to the EDX result. As determined by N₂ sorption, the multishelled Ni–Co oxide particles exhibit a Brunauer–Emmett–Teller (BET) specific surface area of $A = 45 \text{ m}^2 \text{ g}^{-1}$ (Figure S5, Supporting Information). The mass density of NiCo₂O₄ is 5.79 g cm^{-3} , and the mass density of Co₃O₄ is 5.91 g cm^{-3} . Assuming a theoretical density $\rho = 5.7 \text{ g cm}^{-3}$, a freestanding oxide sheet of thickness $t_{\text{theoretical}} = 2/\rho A = 8 \text{ nm}$ would give the same BET specific surface area. It is reasonable to assume that the oxide grain size $D \sim t_{\text{theoretical}}$.

The diameter of multishelled Ni–Co oxide particle can be easily tailored in the range of 500 nm–1.6 μm (Figure S6, Supporting Information) by tuning the CPS diameter via simply adjusting the concentration of metal cations and organic ligand in the reaction medium. Notably, the derived multishelled Ni–Co oxide particles are uniform with similar multilayered structures. Even for the smallest particles with a diameter of about 500 nm, six layers of shells can still be recognized. The apparent thickness of each layer is much larger than $t_{\text{theoretical}} \sim D$ due to the corrugation and porosity of the shell.

To confirm the versatility of the method, Co₃O₄, NiO, and multishelled Ni–Co oxide particles with controlled Ni/Co molar ratios of 1:2 and 2:1 are synthesized (Figure S7, Supporting Information). FESEM characterizations verify that these four types of multishelled particles exhibit similar features in morphology and uniformity. Moreover, TEM images provide direct evidence that multishelled structures are formed for all these four types of hollow particles with some difference in the number of shells and shell thickness. The molar ratio of Ni and

Co elements in each mixed metal oxide material is determined by EDX analysis (Figure S8, Supporting Information).

The carboxylate ligands have been widely demonstrated to be capable of forming coordinate bonds with most transition metal cations and their derived metal carboxylate species can serve as building units toward construction and synthesis of diverse CPs.^[42] Of note, we further verify that this strategy can be applied to the synthesis of other multishelled mixed transition-metal oxide (TMO) particles through the thermal oxidation of mixed transition-metal CP precursors. The multishelled particles of mixed TMOs including manganese cobalt oxide (Mn–Co oxide), manganese nickel oxide (Mn–Ni oxide), zinc manganese oxide (Zn–Mn oxide), and manganese cobalt nickel oxide (Mn–Co–Ni oxide) are obtained. **Figure 2** shows the morphology and interior architecture of these four types of multishelled mixed metal oxide particles. FESEM images confirm that these four types of multishelled particles own similar features in crumpled morphology and size uniformity. Moreover, TEM characterizations provide further evidence that multishelled structures are formed for these four types of hollow particles. The crystal structure and chemical composition of each mixed metal oxide material are verified by XRD (Figure S9, Supporting Information) and EDX (Figure S10, Supporting Information), respectively.

The formation of these multishelled metal oxide particles through the thermal decomposition of CP precursors is mainly based on the heterogeneous contraction caused by heat treatment.^[43] **Figure 3a** schematically illustrates the morphological and structural evolution of the multishelled metal oxide particle from the solid CPS. We take the Ni–Co oxide sample as an example. TEM is used to characterize the intermediates collected at different thermal decomposition stages. The structural change from solid CPS to multishelled mixed metal oxide particle involves several stages (Figure 3b–e). It has to do with the so-called “friable oxide” or oxide spallation phenomena in oxidation, where the large volume change (in this case shrinkage due to the large weight loss of $\approx 75\%$, Figure S11, Supporting Information) from CP to oxide induces residual stress in the oxide layer, and causes spallation once the oxide layer reaches

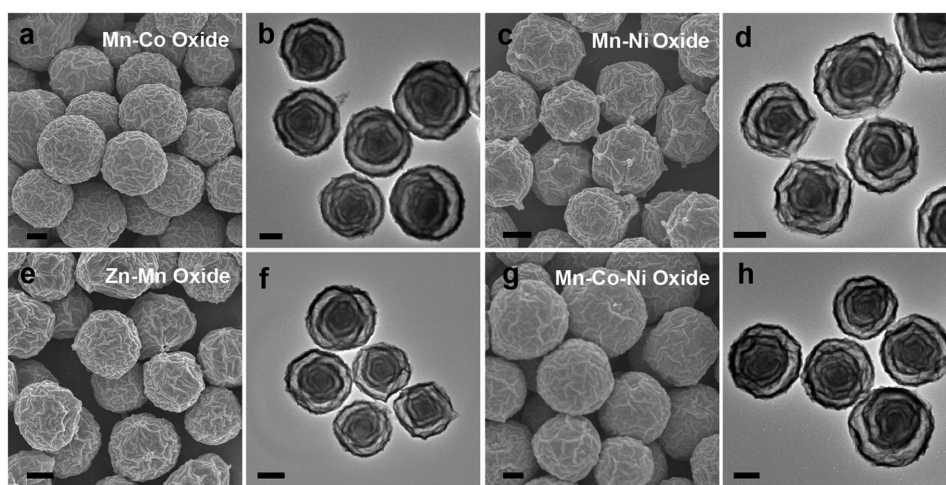


Figure 2. FESEM and TEM images of ternary and quaternary metal oxide multishelled particles. a,b) Mn–Co oxide, c,d) Mn–Ni oxide, e,f) Zn–Mn oxide, and g,h) Mn–Co–Ni oxide multishelled particles. All scale bars are 500 nm.

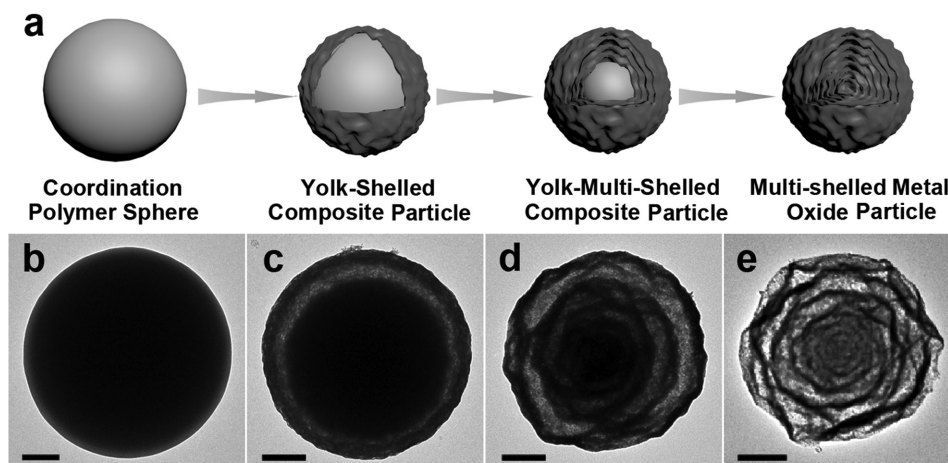


Figure 3. The formation process of the multishelled structure. a) Schematic illustration of the formation process. TEM images of b) Ni–Co CPS and the products obtained after calcination of CPS to different temperatures: c) 360 °C, d) 390 °C, e) 500 °C. The scale bars in (b–e) are 200 nm.

a critical thickness, to form a yolk-shelled structure when the temperature reaches about 360 °C (Figure 3c). Due to residual stress of the phase transformation and adhesion force, the oxide layer has a crumpled morphology. With prolonged heating, the same contraction process continues to take place. A yolk-multi-shelled structure is formed when the temperature is increased to about 390 °C (Figure 3d). By further increasing the temperature to 500 °C, the seven-layered particle is formed (Figure 3e). It is well known that friable oxides tend to have a lot of cracks

within (as they are nonprotective against further oxidation for the metal beneath despite μm thickness, in contrast to the protective SiO_2 , Al_2O_3 , Cr_2O_3 oxide layers that are just sub-10 nm in thickness), so we expect the shells to be partly porous.

We have evaluated the electrochemical properties of the multishelled Ni–Co oxide particles with the Ni/Co molar ratio of 1:1 by using a three-electrode cell in 6.0 M KOH solution. The cyclic voltammetry (CV) curves of the Ni–Co oxide electrode with different sweep rates are shown in Figure 4a. A pair of

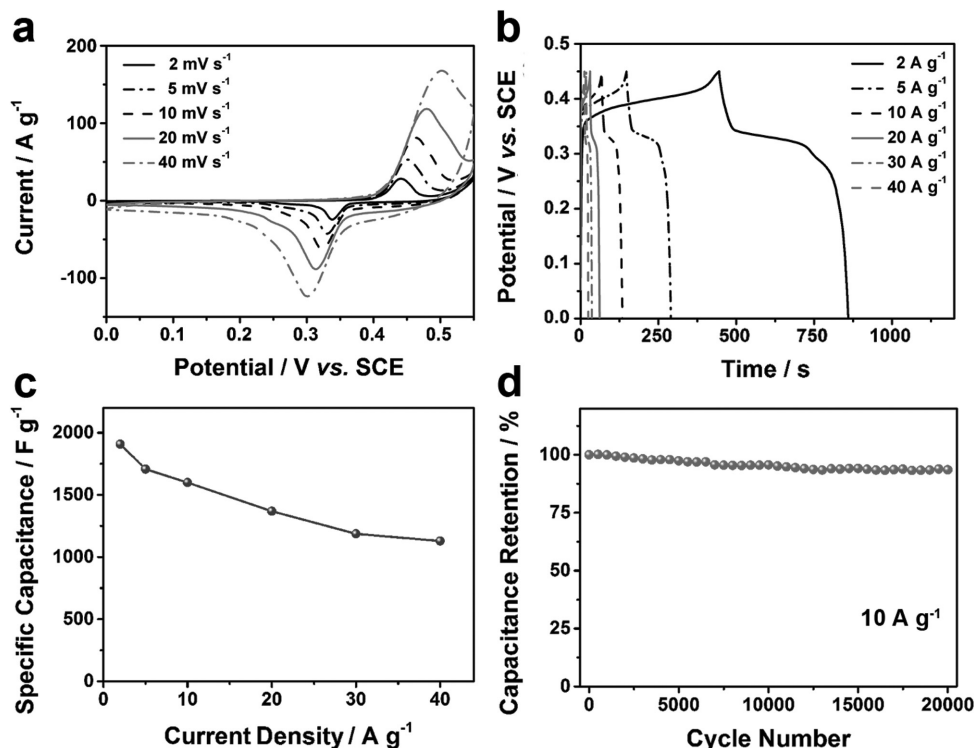


Figure 4. Electrochemical characterizations of the multishelled Ni–Co oxide particles. a) CV curves at different sweep rates. b) Galvanostatic charge-discharge curves at various current densities, and c) the corresponding specific capacitance calculated from the discharge curves. d) The cycling performance at a constant current density of 10 A g⁻¹.

redox peaks can be observed within the potential range from 0 to 0.55 V versus saturated calomel electrode (SCE) at all sweep rates, indicating the presence of Faradaic redox reactions related to $M-O/M-O-OH$ (M represents Ni or Co).^[44,45] Further, from the plots of peak current density (I_p) versus square root of sweep rate ($v^{1/2}$) from 2 to 40 $mV s^{-1}$ for both cathodic and anodic peaks (Figure S12, Supporting Information), the current obeys a power-law relationship with the sweep rate ($I_p = av^b$). Whereas a b -value of 0.5 indicates that the current is controlled by semi-infinite linear diffusion, a value of 1.0 indicates that the current is surface-controlled. For sweep rates ranging from 2 to 40 $mV s^{-1}$, a linear relationship is observed between I_p and $v^{1/2}$ for both cathodic and anodic peaks, indicating that the kinetic is a diffusion-controlled process. Figure 4b presents the galvanostatic charge–discharge curves of the Ni–Co oxide electrode at different current densities ranging from 1 to 40 $A g^{-1}$. In principle, this class of materials gives battery-type conversion electrodes, at least when the grain size D is large. With shrinking D , however, it can gradually transition to pseudocapacitive-type behavior due to rapid surface/interfacial diffusions and facile transformations in the near-interface material.^[46] For the sake of easy comparison to numerous other works in literature, we report here the charge storage capacity in terms of specific capacitance. The calculated specific capacitance as a function of the discharge current density is shown in Figure 4c. A maximum specific capacitance reaches up to 1908 $F g^{-1}$ measured at a discharge current density of 2 $A g^{-1}$, in a voltage scanning window of $\Delta U = 0.45 V$. With the increase of current density, the capacitance of the Ni–Co oxide electrode gradually decreases. The Ni–Co oxide electrode still delivers relatively high specific capacitance of 1707, 1600, 1369, 1187, and 1129 $F g^{-1}$ at current densities of 5, 10, 20, 30, and 40 $A g^{-1}$, respectively. About 71.7% of the capacitance for multishelled Ni–Co oxide particles is retained when the current density increases from 2 to 20 $A g^{-1}$. The cycling performance of the Ni–Co oxide electrode is evaluated by the continuous charging–discharging test at a current density of 10 $A g^{-1}$ (Figure 4d). Impressively, the multishelled Ni–Co oxide particles manifest exceptional cycling stability and deliver 93.6% of its initial capacitance even after 20 000 cycles. After cycling, the multishelled structure can be well retained (Figure S13, Supporting Information). The multishelled Ni–Co oxide particles with the Ni/Co molar ratio of 1:2 also exhibit similar rate capability and cycling performance (Figure S14, Supporting Information). The electrochemical performance of multishelled Ni–Co particles is superior to that of many Ni–Co based metal oxides and other mixed metal oxide materials (Table S1, Supporting Information), which must be related to advantageous structural features of the multishelled Ni–Co oxide particles, to be discussed next.

To further evaluate the Ni–Co oxide electrode for practical applications, a hybrid supercapacitor (HSC) device is fabricated using the Ni–Co oxide electrode as the cathode and graphene/multishelled mesoporous carbon sphere (G/MMCS) composite electrode (Figure S15, Supporting Information) as the anode in 6.0 M KOH solution (Figure 5a). The typical CV curves of the Ni–Co oxide//G/MMCS HSC device at various sweep rates between 0 and 1.6 V are shown in Figure 5b. A combination of both pseudocapacitive and electric double-layer types of

capacitance can be seen at all sweep rates. Figure 5c reveals the galvanostatic charge–discharge profiles at different current densities. The discharge curves are almost symmetrical to the corresponding charge curves, suggesting excellent charge-storage reversibility of the HSC device. Figure 5d shows the specific capacitance calculated from the discharge curves. The Ni–Co oxide//G/MMCS HSC device achieves a relatively high specific capacitance of 149 $F g^{-1}$ (based on active materials weight) at a current density of 2.0 $A g^{-1}$. Moreover, the HSC device exhibits excellent rate capability with 82.5% of capacitance retained even at the current density of 20 $A g^{-1}$. The cycling performance of the HSC device at a current density of 10 $A g^{-1}$ is shown in Figure 5e. Remarkably, the HSC device manifests very high cycling stability and is able to deliver 91.3% of its initial capacitance even after 10 000 cycles. The Ragone plots of Ni–Co oxide//G/MMCS HSC device derived from the discharge curves are shown in Figure 5f. Impressively, a high energy density of 52.6 $Wh kg^{-1}$ can be obtained at a power density of 1604 $W kg^{-1}$ and the energy density still retains 29.6 $Wh kg^{-1}$ even at higher power density of 28 800 $W kg^{-1}$, which show enhanced electrochemical performance compared with many previously reported hybrid systems (Table S2, Supporting Information), such as Ni_xCo_{1-x} oxide//AC,^[47] Co_3O_4 //AC,^[48] $Ni(OH)_2$ -CNT//AC,^[49] and $NiCo_2S_4$ //G/CS.^[8]

Strain accommodation is a well-recognized essential problem in battery-type conversion electrodes.^[50] It is extremely intriguing to consider how the transformation strains are accommodated very rapidly for tens of thousands of cycles in pseudocapacitor electrodes, in a supposedly brittle ceramics. Figure 4b shows that 2 $A g^{-1} \times 420 s = 230 mA h g^{-1}$ of charge can be reversibly taken in and out of the electrode very quickly, for 20 000 cycles. This large amount (comparable to advanced battery cathode materials) cannot be just surface charge storage, and insertion of ions and interior redox of Ni, Co cations in the grains (could be in near-surface or near-grain boundary regions, considering $D \sim t_{theoretical} = 8 nm$) must be involved. Previously, with electrochemical quartz crystal microbalance, it was determined that insertion/extraction of multiple water molecules often accompany one redox reaction in aqueous pseudocapacitor materials.^[51] Assuming a volume change of just 0.5 water molecule ($\approx 15 \text{ \AA}^3$) per redox electron transfer, this would still require a volume expansion $\Delta V/V \approx 30\%$ of the hydrated metal oxide. How can fragile-looking structures like Figure 1c,d accommodate the huge expansion and shrinkage of Ni–Co oxide grains is the mystery we want to reveal with in situ liquid-cell TEM.

We next conduct in situ TEM observation to understand the charge/discharge process of multishelled Ni–Co oxide particles. A liquid confining cell^[52] is used to encapsulate the aqueous electrolyte preventing it from evaporating in the high vacuum inside TEM. The multishelled Ni–Co oxide particles are used as the cathode and W metal as the anode in 6.0 M KOH solution. A constant voltage charge/discharge is performed by repeating 20 s of charge biased at 1.0 V on the Ni–Co oxide versus W electrode and 20 s of discharge at $-0.3 V$. Figure 6a shows the change in the Ni–Co oxide particle during the charge/discharge process (see also Movie S1, Supporting Information). Only small apparent volume expansion and contraction of the shell are observed during the cycling. The outer shell

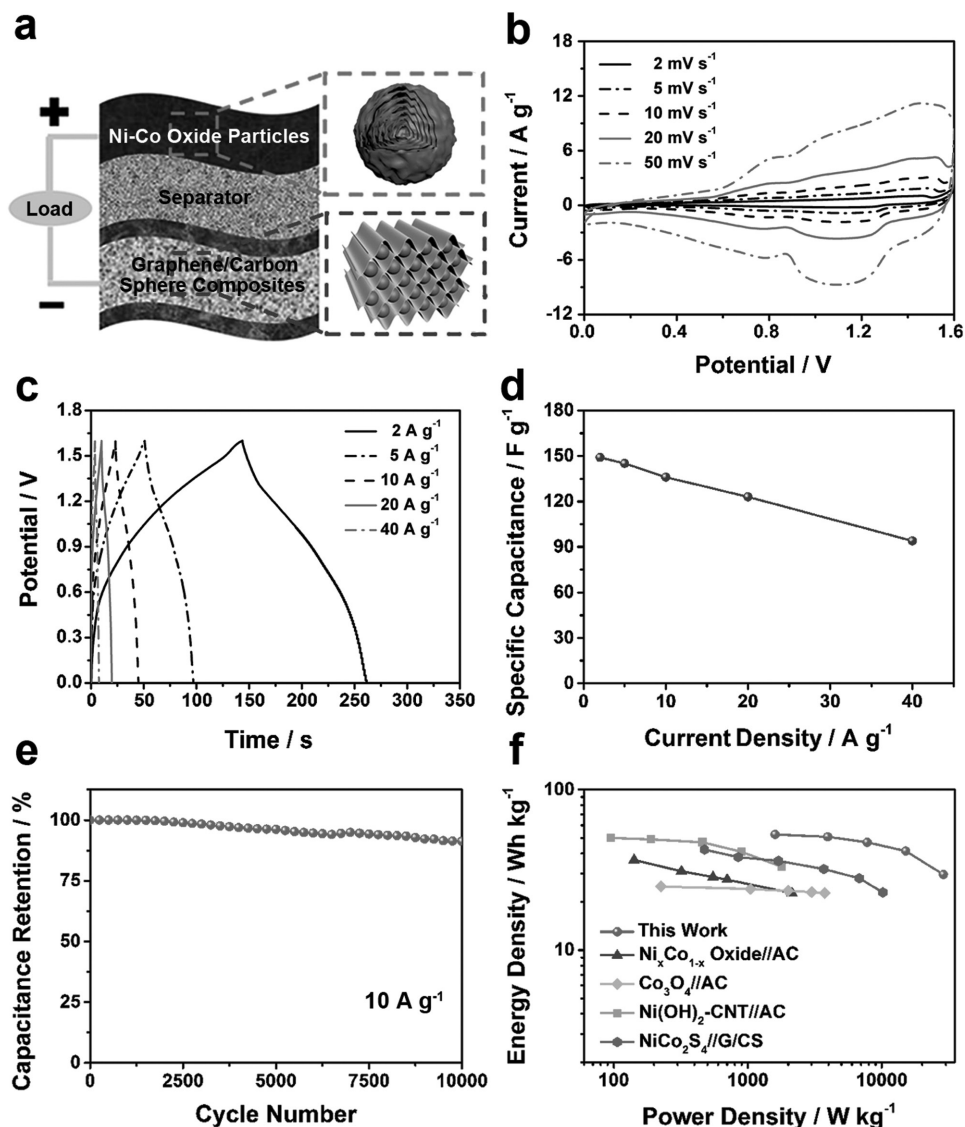


Figure 5. Electrochemical evaluation of the Ni–Co oxide//G/MMCS HSC device. a) Schematic illustration of the HSC device. b) CV curves at different sweep rates. c) Galvanostatic charge/discharge voltage profiles at various current densities, and d) the corresponding specific capacitance calculated from the discharge curves. e) The cycling performance and f) Ragone plot of the HSC device.

bulges a bit upon charge, which shrinks back at discharge, as indicated by the arrowheads in the figure. Figure 6b shows the change in the Ni–Co oxide particle diameter/during the cyclic charge/discharge. The change is within a few percent, but slight increase in the particle diameter is observed as the cycle number is increased. This change may be associated with the change in the wrinkle pattern of the shell. It is also highly likely that the shells are porous, so the void spaces in the grain aggregation can accommodate the substantial volume change of individual grains due to Faradaic redox reactions, related to $M-O/M-O-OH$ (M represents Ni or Co) and water insertion/extraction.^[44,45] Such well-accommodated volume changes at nanograin level are seen to drive only minimum overall structural alteration of the multishelled particles, during rapid charging/discharging, contributing to the extremely high cyclability of the electrode.

To explore the structural stability limit of the multishelled particles, we applied a higher voltage (still before electrolyte decomposition and gas evolution, which we have seen at higher and lower voltages, see Movie S2 (Supporting Information) at 2.0 V and Movie S3 (Supporting Information) at -0.7 V). Figure 6c shows the change in the multishelled Ni–Co oxide particle charged at 1.4 V (see also Movie S4, Supporting Information). The shells disintegrate to smaller particles and scatter into the electrolyte. The highly concentrated OH^- ions on the nanoparticles may cause repulsion between them and eventually destroy the shell structure as schematically illustrated in Figure 6d. Multiple factors such as applied voltage, current density, and the structure of the multishelled particles (nanoparticle size, packing density, etc.) need to be considered to understand the criteria to initiate this failure, which is not the focus of the present work. The explosion of the particle shown

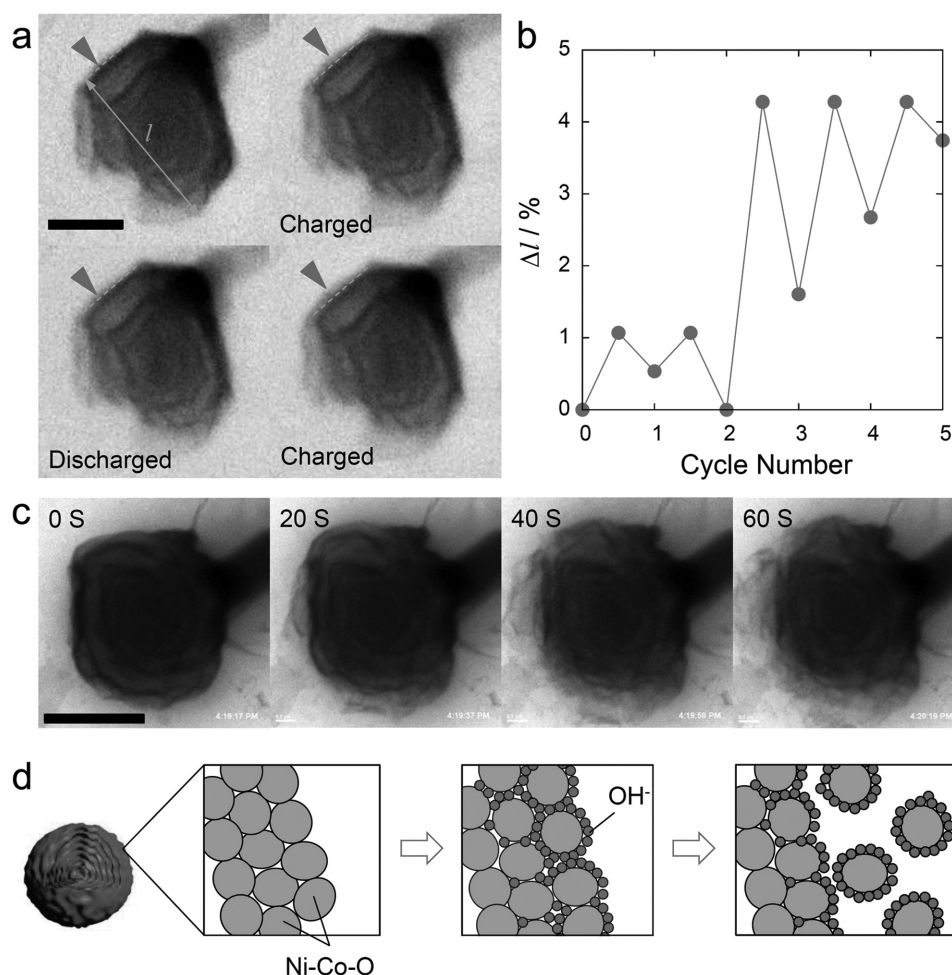


Figure 6. In situ liquid-cell TEM observation of charge/discharge process. a) Change in the multishelled Ni–Co oxide particle shape in the charge/discharge process. The arrow heads indicate the bulging of the outer shell. The dashed line is the guide for the eyes. See also Movie S1, Supporting Information. b) The particle size evolution in the repeating charge/discharge cycles. c) Fracturing of the particle during charge. See also Movie S4, Supporting Information. d) Schematic illustration explaining the nanoparticle dissociation from the shell. The scale bars in (a) and (c) are 1 μm .

here may be the extreme case. But detachment of individual nanoparticles from the shell at lower voltages can still be one of the factors causing the irreversible capacity loss. The scattered nanograins are very small, with sub-10 nm grain size D . Such extremely small grain sizes and porous shell would support prolific and percolating surface/interfacial diffusion pathways and facile transformations in the near-interface material^[53] and pseudocapacitive-type behavior.^[46] The excellent strain accommodation at the shell level and structural integrity of the multishelled particle despite the necessarily large volume expansion of the nanograins, revealed by in situ TEM before the disintegration voltage, gives a microscopic explanation for the excellent cyclability (10^4 cycles, much better than typical battery-type electrodes) of our electrode, that apparently possesses similar charge storage ability as advanced battery cathode materials ($\approx 230 \text{ mAh g}^{-1}$).

In summary, a general method is developed to prepare highly complex multishelled mixed metal-oxide particles. The key feature of the new method is that a novel class of amorphous coordination polymers serves as the precursors for the effective

formation of various multishelled mixed metal-oxide particles by a subsequent thermal treatment. This provides the platform for making many designed multishelled metal oxide particles with tailored size, number of shell layers, and composition. As a demonstration, the multishelled Ni–Co oxide particles exhibit exceptional charge storage capability in aqueous electrolyte with high specific capacitance ($\approx 1900 \text{ F g}^{-1}$ at 2 A g^{-1}), good rate capability, and ultrahigh cycling stability (93.6% retention over 20 000 cycles). A hybrid supercapacitor against graphene/multishelled mesoporous carbon sphere shows a high energy density of 52.6 Wh kg^{-1} at a power density of 1604 W kg^{-1} (based on active materials weight), as well as remarkable cycling stability. As demonstrated by the liquid-cell in situ transmission electron microscopy observation, the volume change of the oxide nanograins is well-accommodated at the shell level during the charge/discharge process in alkaline electrolyte, which is believed to be the reason for the remarkable electrochemical performance and longevity. The present recipe offers a new way to precisely control the structure and composition of multishelled metal oxide particles for a wide range of applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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