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ARTICLE TYPE

Self-powered Electrochemical Deposition of Cu@Ni(OH)₂ Nanobelts for High Performance Pseudocapacitors

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Two aluminum-driven spontaneous electrochemical reactions are developed for depositing Cu@Ni(OH)₂ nanobelts on carbon/aluminum electrodes. The Cu@Ni(OH)₂ NBs function as pseudocapacitor electrodes, which exhibit a high specific capacitance of 2426 F g⁻¹ and a remarkable rate performance.

Pseudocapacitors are attracting considerable interest, because of their high capacitance, rapid recharging and high power density, which overcome the limitations of conventional batteries and capacitors in electrochemical reactions.^{1, 2} As is widely known, transition metal oxides³⁻⁸ and hydroxides⁹⁻¹², as well as electronically conducting polymers^{13, 14} with multiple oxidation states, resulting in rich redox reactions, are ideal electrode materials use in pseudocapacitors. Nickel hydroxide (Ni(OH)₂) is an extensively used material for storing energy, because of its abundance, low cost, and high theoretical specific capacitance.¹⁰⁻¹² However, its insufficient electrical conductivity and short cycle life severely limit its usefulness.¹⁵ Coating Ni(OH)₂ onto three dimensional (3D) conductive substrates shortens the electron transport distance^{11, 12} and substitutes some cations (such as Co) for Ni, substantially improving rate capability and cycleability.^{16, 17} However, substrate preparation and the subsequent Ni(OH)₂ decoration are typically complex and consume much energy. Owing to the global energy crisis, a simple and environmentally friendly means of fabricating high-performance electrodes is sought urgently.

Generally known as immersion plating, galvanic displacement is superior to high temperature processes in many ways, including the relative simplicity of the procedure, the inexpensive equipment required and the low operating temperature.¹⁸⁻²¹ Unlike electrodeposition, galvanic displacement does not require an external power supply, but is driven by spontaneous dissolution of the sacrificial metal anode, which is accompanied by a reduction of coupled metal ions on the surface of the anode. However, galvanic displacement is frequently performed to synthesize hollow nanomaterials because the core anode typically functions as a sacrificial template or is encapsulated in coating shell, limiting its reuse.²¹⁻²³ Our recent work presented the efficient growth of copper nanobelts (NBs) and nanorods on a conducting substrate rather than on Al foil itself in a normal galvanic displacement. This tendency can be exploited to coat Ni(OH)₂ on CuNBs through a further electrochemical reaction of

the uncovered Al.

This work develops a two-step aluminum-driven spontaneous electrochemical deposition method, which includes the growth by galvanic displacement of a core of copper nanobelts (CuNBs) and the subsequent precipitation of a shell of Ni(OH)₂ nanosheets on the CuNBs. The proposed method is characterized by a relatively simple soaking process without the need for a power supply, as well as the formation of highly conductive 3D CuNBs interlacing networks that function as an excellent current collector. To the best of our knowledge, this work is the first to form a core-shell structure *via* two electrochemical reaction of the sacrificial Al anode. Importantly, the proposed method is scalable and conducive to mass production. Moreover, the Cu@Ni(OH)₂ NBs electrodes herein exhibit an excellent specific capacitance and remarkable rate capability. Moreover, the rate performance and capacitance retention are further improved by partially substituting Ni with Co.

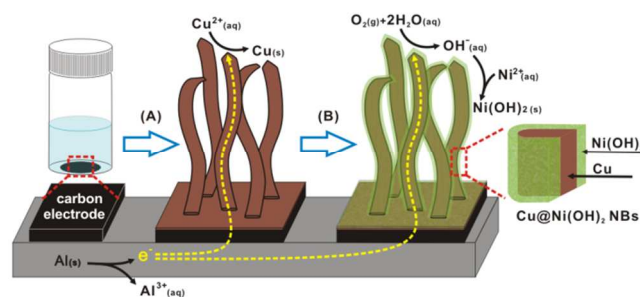


Fig.1 Fabrication of Cu@Ni(OH)₂ nanobelts on carbon/aluminium.

Cu@Ni(OH)₂ NBs on C/Al substrate were synthesized by a unique two-step spontaneous electrochemical deposition procedure, which is schematically depicted in Figure. 1. The procedure includes (a) the galvanic deposition of CuNBs on the carbon side of the C/Al substrate by immersing it into an aqueous solution of CuCl₂, CTAC and HNO₃, and (b) the coating of Ni(OH)₂ nanosheets onto the surfaces of CuNBs by further immersing them into aqueous NiSO₄. In this two-step deposition process, Al foil has a critical role in both steps. The growth of CuNBs is based on a galvanic reduction of Cu and Al, which occurred spontaneously herein, because of the positive redox potential between Cu²⁺ and Al (Eq.1). An earlier work proposed the growth pathway for CuNBs.¹⁸ Tiny hydrogen gaseous bubbles were also detected after 18 h and adsorbed on the surface of Al

foil (Eq. 2). Ni(OH)₂ nanosheets precipitated on CuNBs in an aqueous solution of NiSO₄, owing to a local increase in the pH there by a redox reaction between oxygen and Al. (Eqs. 3, 4).

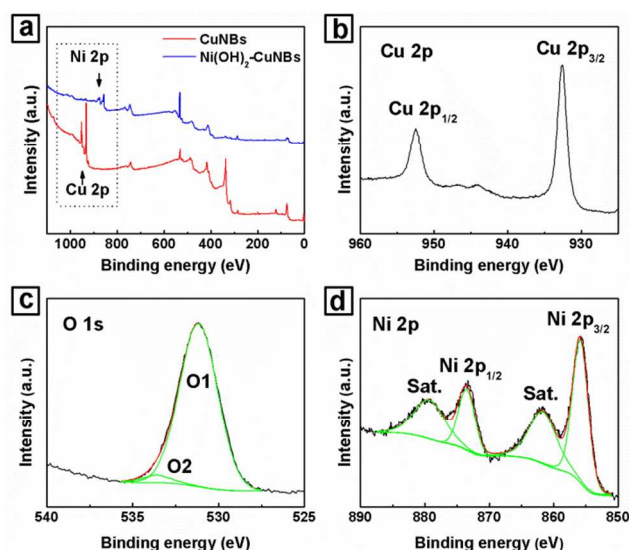
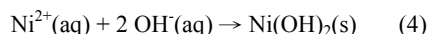
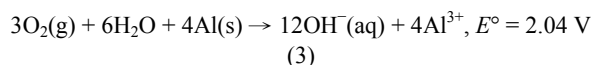
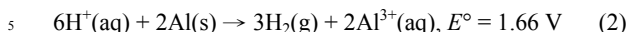
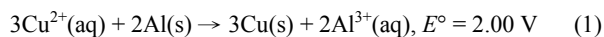


Fig. 2 (a) XPS survey of CuNBs, and Cu@Ni(OH)₂ NBs, (b) XPS peaks of Cu 2p of pristine CuNBs, (c) XPS peaks of Ni 2p of Cu@Ni(OH)₂ NBs, and (d) XPS peaks of O 1s of Cu@Ni(OH)₂ NBs.

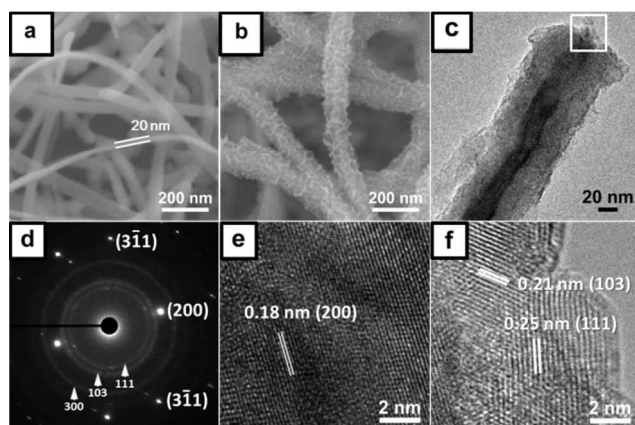


Fig. 3 SEM images of CuNBs (a), Cu@Ni(OH)₂ NBs (b); TEM images (c) and SAED patterns (d) of Cu@Ni(OH)₂ NBs, high-resolution TEM (HRTEM) images of Cu core (e), and Ni(OH)₂ shell (f).

The phase structure of the CuNBs on the C/Al substrate is determined using X-ray diffraction (XRD) (Fig. S1). The XRD reflection pattern demonstrates that the NBs comprise face-centered cubic (fcc) Cu (JCPDS 89-2838). The constant peak position indicates that the Ni(OH)₂ coating process does not change the phase structure of CuNBs. No peak of Ni(OH)₂ is obtained, probably because of the insufficient crystallinity of

Ni(OH)₂ that was deposited on the surface of the CuNBs.

Figure 2a displays the full-range X-ray photoelectron spectra (XPS). The pristine CuNBs yields two strong peaks, and no satellite peak for cupric oxide (CuO) is obtained (Fig. 2b). The peaks at 932.4 and 952.2 eV that are associated with Cu 2p_{3/2} and Cu 2p_{1/2} photoelectrons may be attributed to metal Cu or cuprous oxide (Cu₂O) because of their very close binding energies (Fig. 3b).²⁴ Based on our earlier investigation, transmission electron microscopic (TEM) analysis suggested the presence of a minute quantity of Cu₂O on the surface of the CuNBs.¹⁸ In Fig. 3c, two oxygen bonds are seen in the O 1s spectrum: O1 at 531.2 eV is associated with nickel-oxygen bonds, and O2 at 533.9 eV is associated with the oxygen in the physis- and chemisorbed water.²⁵ Figure 3d displays the Ni 2p XPS spectrum, in which the typical Ni²⁺ 2p_{3/2} and 2p_{1/2} peaks with two shakeup satellites (denoted as “Sat.”) are observed at 855.9 and 873.4 eV,²⁵ respectively. Characteristic of an Ni(OH)₂ phase, the spin energy separation of 17.5 eV is consistent with previously reported data concerning Ni 2p_{3/2} and Ni 2p_{1/2} in Ni(OH)₂.^{10, 11}

Figure 3 displays the field-emission scanning electron microscopic (SEM) and TEM images of the as-prepared samples. Figure 3a presents the pristine CuNBs that are several tens of mm long and ~ 20 nm thick. The CuNBs grew densely and covered the carbon electrode surface, ultimately forming an interlacing network (Fig. S2a). An energy-dispersive spectrum (EDS) demonstrates that the NBs comprise mostly Cu (Fig. S2b). The Cl signal arises from the adsorption of CTAC on CuNBs and the carbon electrode. Figure 3b presents the SEM images of samples following the deposition of Ni(OH)₂. The belt-like morphology is retained and the Ni(OH)₂ nanosheets are uniformly coated on the surface of the CuNBs. EDS analysis confirms that the core-shell NBs comprise Cu, Ni and O (Fig. S3a). Figure S3b plots the relative mass of Ni(OH)₂ that is loaded on the CuNBs as a function of time, determined from the difference between the NiSO₄ concentrations between before and after coating with Ni(OH)₂ by inductively coupled plasma (ICP).

The structure and crystallinity of Cu@Ni(OH)₂ NBs are more closely characterized by TEM. Figure 3c presents a low-magnification bright-field image of Cu@Ni(OH)₂ NBs. The surface of CuNB is entirely covered by Ni(OH)₂ nanosheets with a thickness of ~ 20 nm (Fig. S4). Figure 3d presents the corresponding selected area electron diffraction (SAED) pattern, which includes both strong spots and weak rings. The *d* spacing, estimated from the spots that are closest to the center of the beam, is 0.18 nm, which is the *d* spacing of Cu (200) planes (JCPDF 89-2838). The lattice parameter *a* is thus determined to be 0.36 nm, which is similar to the previously reported value for fcc Cu. From the above patterns, the crystallographic zone axis is [001]. The *d* spacings from the rings are 0.25, 0.22 and 0.16 nm, which are consistent with the (111), (103) and (300) planes of α-3Ni(OH)₂·2H₂O (JCPDS 22-0444), indicating the formation of a polycrystalline α-Ni(OH)₂ shell. Figure 3e-f presents high-resolution TEM images of the belt tip that is indicated in Fig. 3c. The lattice fringes yield interplanar spacings of 0.18, 0.21 and 0.25 nm of Cu (200), α-Ni(OH)₂ (103) and (111), respectively.

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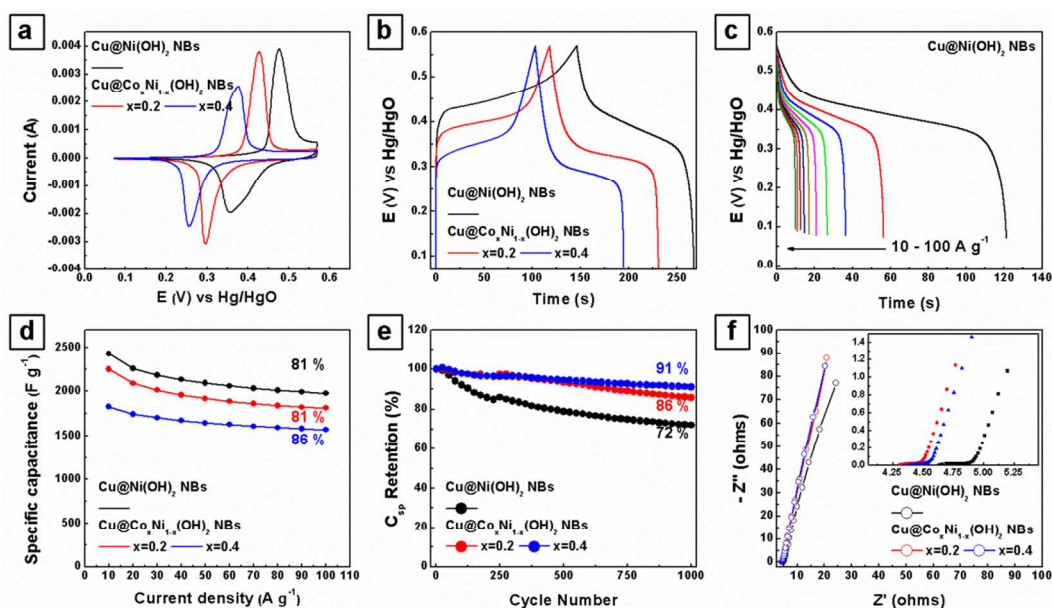


Fig. 4 (a) CV curves of Cu@Ni(OH)₂ NB and Cu@Co_xNi_{1-x}(OH)₂ NB (x=0.2 and 0.4) electrodes obtained at a scan rate of 5 mV s⁻¹. (b) Galvanostatic charge-discharge curves at 10 A g⁻¹ for Cu@Ni(OH)₂ NB and Cu@Co_xNi_{1-x}(OH)₂ NB electrodes. (c) Galvanostatic charge-discharge curves for Cu@Ni(OH)₂ NB electrode at various current densities (10–100 A g⁻¹). (d) Corresponding specific capacitance of Cu@Ni(OH)₂ NB and Cu@Co_xNi_{1-x}(OH)₂ NB electrodes at increasing current densities. (e) Retained specific capacitance of Cu@Ni(OH)₂ NB and Cu@Co_xNi_{1-x}(OH)₂ NB electrodes as functions of number of cycles, obtained at a scan rate of 30 A g⁻¹. (f) Comparison of Nyquist plots of electrodes made with Cu@Ni(OH)₂ NBs and Cu@Co_xNi_{1-x}(OH)₂ NBs.

Cu@Ni(OH)₂ NBs are used as the electrode material in the pseudocapacitor for the following reasons. (a) The 3D web of encapsulating CuNBs provides a highly conductive network with a large surface area that promotes electron transport to the Ni(OH)₂ shell; (b) the thin Ni(OH)₂ nanosheet structure shortens ion diffusion paths and facilitates the migration of electrolyte ions at a large current density, and (c) the polymeric binder-free electrode prevents blocking of the surface of active materials. The electrochemical properties of Cu@Ni(OH)₂ NBs are studied using a three-electrode system in aqueous 1 M KOH in a potential range of 0.07–0.57 V vs. Hg/HgO.

Figure 4a plots the CV curves of Cu@Ni(OH)₂ NBs obtained at a scan rate of 5 mV s⁻¹. This figure includes a pair of redox peaks, which correspond to the Ni(OH)₂ redox reaction. The anodic and cathodic peaks at ~ 0.50 and ~ 0.35 V, respectively, are attributable to the reversible Faradaic redox reactions between Ni(OH)₂ and NiOOH (Eq. 5).



The specific capacitance of this electrode is calculated from the CV curve to be 2608 F g⁻¹. The galvanostatic charge-discharge behavior of the electrode is studied between 0.07 and 0.57 V at a current density of 10 A g⁻¹. The nonlinear charge-discharge curves in Fig. 4b clearly reveal pseudocapacitive behavior. Additionally, the discharge curve does not exhibit an obvious iR drop, indicating that the electrode has a low internal resistance.

The specific capacitances of the Cu@Ni(OH)₂ NB electrode is calculated to be 2426 F g⁻¹. Figure 4c plots the discharging curves of Cu@Ni(OH)₂ NBs that are obtained at current densities from 10 to 100 A g⁻¹. Figure 4d shows the specific capacitances that are calculated from the curves in figure 4c. The Cu@Ni(OH)₂ NBs exhibit an excellent specific capacitance retention of 81 % at a current density of 100 A g⁻¹, which is markedly higher than those obtained in earlier works on pure Ni(OH)₂, suggesting an excellent rate capability. (See Table S1 in Supporting Information.) The rate performance benefits from the ability of the encapsulated copper NBs to support efficient electron transport and the shortening of the ion diffusion paths by the thin Ni(OH)₂ nanosheets.

The long-term cycling performance of the Cu@Ni(OH)₂ NB electrode is evaluated over 1000 galvanostatic charge-discharge cycles at 30 A g⁻¹. As shown in Fig. 4e, the fading of the capacitance (with 72% remaining) of Cu@Ni(OH)₂ NBs may be related to the expansion and shrinkage of the layered structures of the hydroxide under the repeated charge-discharge process.¹⁷ However, the performance is comparable with that obtained in previous works on pure Ni(OH)₂.

The enhanced electronic transport in Cu@Ni(OH)₂ NBs electrodes is examined further by performing an electrochemical impedance spectroscopy (EIS) analysis. Figure 4f presents the Nyquist plots of the as-prepared Cu@Ni(OH)₂ NB electrode that are obtained at the oxidation peak potential at frequencies from

10^5 to 10^{-1} Hz. The spectra are almost vertical at a low frequency with no semicircle at high frequency, indicating good capacitive behavior. The absence of a semicircle in the high-frequency region suggests a small electrode resistance and high rate of charge transfer between the electrolyte and the active material during the charge storage and delivery processes. Figure S5 present the Nyquist plot of the Cu@Ni(OH)₂ NB electrode after 250 cycles. The small semicircle indicates increased charge-transfer resistance, which may be the cause of the fading of the capacitance during long-term cycling.

Finally, following the literature,¹⁷ nickel is partially substituted with cobalt (Co), which is commonly used to increase the conductivity and stability of Ni(OH)₂ electrodes. Figure 4a also plots the CV curves of the Cu@Co_xNi_{1-x}(OH)₂ NBs (x= 0.2 and 0.4). The redox peak is related to the redox reactions of both cobalt and nickel hydroxide. This figure reveals no redox peak separation, indicating thorough mixing of Co-Ni binary hydroxide. The peak shifts to a lower potential as the Co content of the binary hydroxide increases. This shift in the potential of the discharge plateau is correlated closely with the CV results (Fig. 4b). The specific capacitances of these electrodes are 2250 and 1828 F g⁻¹. The Cu@Co_{0.4}Ni_{0.6}(OH)₂ NBs exhibit a 6% improvement rate capacitance than Cu@Ni(OH)₂ NBs (Fig. 4d), which is attributed to the increase in shell conductivity as the amount of conductive Co(OH)₂ increases relative to the amount of Ni(OH)₂.¹⁷ The Cu@Co_{0.4}Ni_{0.6}(OH)₂ NBs also exhibit a greater capacitance retention of 91% during long-term cycling. The enhanced electrochemical properties are verified by the Nyquist plots, in which the straight line portions for Cu@Co_xNi_{1-x}(OH)₂ NBs (x= 0.2 and 0.4) are closer to the vertical spike than Cu@Ni(OH)₂ NBs in the low-frequency region, indicating that cobalt substitution further improves the capacitive behavior. Additionally, the effective retention of the low charge-transfer resistance of the Cu@Co_{0.4}Ni_{0.6}(OH)₂ NB electrode during cycling reflects the improved cycleability (Fig. S5).

Conclusions

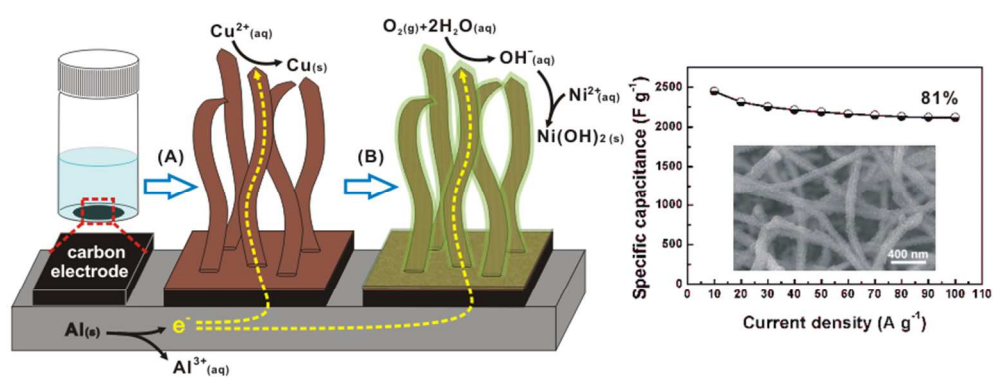
This work develops a cost-effective method of fabricating supercapacitors that demonstrates the feasibility of using Cu@Ni(OH)₂ NB electrodes for supercapacitors. Highly dense hybrid nanomaterials are prepared by aluminum-driven electrochemical deposition, which involve the galvanic deposition of CuNBs followed by coating a shell of uniform Ni(OH)₂ nanosheets onto the CuNB surfaces. The as-prepared electrode has a high C_{sp} of 2426 at 10 A g⁻¹ and an excellent (rate performance of 1977 F g⁻¹, even at 100 A g⁻¹). The electrochemical properties are enhanced by the ability of the encapsulated copper NBs to support rapid electron transport and by the shortening of ion diffusion paths by a thin Ni(OH)₂ nanosheet. Importantly, Cu@Ni(OH)₂NBs are highly promising materials for use in the next generation of high-performance supercapacitors. Moreover, the rate performance and long-term cyclic stability of these NBs can be further improved by substituting some of the Ni for Co and forming the more conductive Co(OH)₂.

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Notes and references

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Aluminum-driven spontaneous electrochemical depositions
79x31mm (300 x 300 DPI)