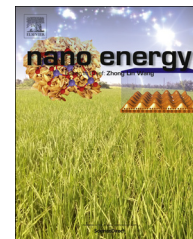




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COMMUNICATION

A flexible all-solid-state micro-supercapacitor based on hierarchical CuO@layered double hydroxide core-shell nanoarrays



Zhenhua Li, Mingfei Shao*, Lei Zhou, Ruikang Zhang, Cong Zhang, Jingbin Han, Min Wei*, David G. Evans, Xue Duan

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

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Abstract

Flexible and lightweight wire-shaped supercapacitors (WSSCs) have recently attracted increasing interest, due to their versatility in the device design and application potentials in portable or wearable electronics. However, practical applications of WSSCs are still limited by the relatively poor performances, owing to the challenges in the rational modification of one-dimensional (1D) substrates with sophisticated nanostructure. Herein, we demonstrate a WSSC by virtue of material exploration and fabrication strategy. A 1D nanoarray electrode consisting of CuO nanowires core and CoFe-layered double hydroxide (CoFe-LDH) nanoplatelets shell supported on a copper wire is prepared with fine control over the structure/morphology, which displays a largely improved specific capacitance, high rate capability and long cycling lifespans. Based on this sophisticated core-shell nanostructure, a flexible all-solid-state asymmetric WSSC was fabricated, which exhibits excellent supercapacitive performances with a high energy density ($1.857 \text{ mWh cm}^{-3}$) and long-term cycling stability (99.5% device capacitance retention over 2000 cycles). By virtue of the versatility of metal wire substrates, transition metal oxides and LDHs materials, the synthesis strategy presented here can be extended to the fabrication of other portable and flexible micro energy storage devices.

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*Corresponding authors.

Tel.: +86 10 64412131; fax: +86 10 64425358.

E-mail addresses: shaomf@mail.buct.edu.cn (M. Shao),
weimin@mail.buct.edu.cn (M. Wei).

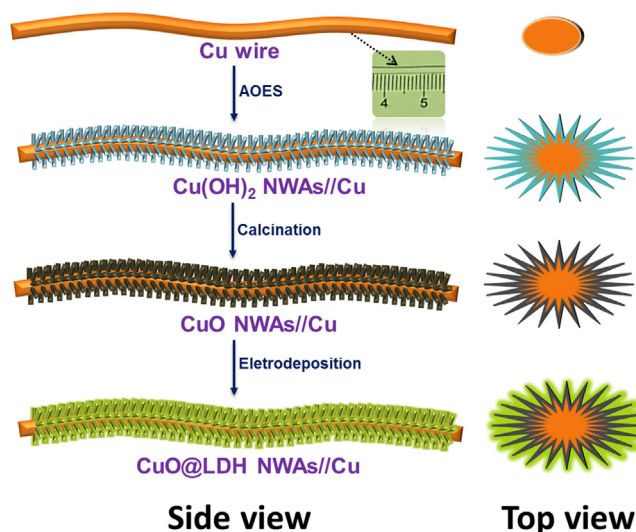
Introduction

With increasing demands for the next-generation portable electronics such as roll-up displays, photovoltaic cells as

well as wearable devices, the development of flexible, lightweight, and environmentally friendly energy storage equipment has attracted considerable attention [1-4]. As one type of the flexible energy storage devices, wire-shaped supercapacitors (WSSCs) have become a research focus recently, due to their freedom in the device design and application potentials in wearable electronics [5-8]. Since the first prototype of WSSC made from ZnO nanowires by Wang and co-workers [9], various linear substrates (e.g., carbon materials [10,11], metal oxides [12,13] and conducting polymers [14,15]) have been widely studied towards WSSCs. However, practical applications of WSSCs are still hindered by the relatively poor performance of the electrode materials, such as low energy density and short charge/discharge lifespans. As a result, further efforts are still urgent to tackle these problems from the viewpoint of electrode materials exploration and fabrication strategy.

One-dimensional (1D) nanowire arrays (NWAs) with core-shell architecture have attracted considerable attention in the energy storage due to the ingenious combination of an efficient exposure of active sites and synergetic effect between core and shell [16-20]. In the past decades, various materials including carbons [21,22], metal oxides/hydroxides [23,24] and conducting polymers [25,26] have been integrated into this kind of core-shell structures. For instance, transition metal oxides/hydroxides grafted on the surface of 1D carbon fibers [27] or CNTs [28] have been reported with excellent performance in supercapacitors. Moreover, 1D metal oxides/hydroxides serving as core to induce the growth of electroactive species shell for enhanced supercapacitive properties (e.g., $\text{Co}_3\text{O}_4@\text{NiO}$ [29], $\text{TiO}_2@\text{PANI}$ [30], $\text{NiCo}_2\text{O}_4@\text{Ni}_3\text{S}_2$ [31] core-shell arrays) were also investigated. Although much progress has been made, most of recent electrodes based on 1D core-shell structure are constructed on conductive plane- or foam-like substrates, which is not applicable to the advanced 1D micro-devices. Therefore, how to achieve the rational design and facile fabrication of wire-shaped micro-supercapacitors with enhanced energy storage performance still remains a challenge.

Layered double hydroxides (LDHs), which are composed of positively-charged brucite-like host layers and charge-compensating interlayer anions, have been used as promising candidates in electrochemical energy storage/conversion owing to their tunable chemical composition, cost effectiveness and environmentally friendly nature [32-35]. Herein, we present the design and fabrication of well-aligned CuO@LDH core-shell NWAs on a gracile copper wire substrate via a three-step procedure (Scheme 1): (1) the synthesis of $\text{Cu}(\text{OH})_2$ NWAs on copper wire, (2) chemical transformation of $\text{Cu}(\text{OH})_2$ to CuO NWAs by heat treatment, followed by (3) a further electrosynthesis of LDH shell on the surface of CuO NWAs. The as-obtained core-shell NWAs consisting of CuO core and intercrossing LDH nanoplatelets shell can be finely controlled over the shell thickness and morphology, which display a largely improved specific capacitance, higher rate capability and longer cycling lifespans, much superior to those of pristine CuO and LDH NWAs. Based on this core-shell nanostructure, a flexible all-solid-state asymmetric WSSC is fabricated, which exhibits a wide voltage range of 1.2 V, high areal energy density of $93.75 \mu\text{Wh cm}^{-2}$ (volumetric energy density of



Scheme 1 Schematic illustration for the fabrication of hierarchical CuO@CoFe-LDH core-shell NWAs supported on the copper wire.

$1.857 \text{ mWh cm}^{-3}$), as well as long term cyclability (over 99% device capacitance retention after 2000 cycles).

Experimental Section

Preparation of CuO nanowire arrays (NWAs)

The CuO nanowire arrays (NWAs) were prepared by using a method reported previously [36]. Typically, a Cu wire with a diameter of 0.3 mm (surface area: $0.0942 \text{ cm}^2 \text{ cm}^{-1}$; volume: $0.0007 \text{ cm}^3 \text{ cm}^{-1}$) was pretreated with 2 M HCl solution, absolute ethanol, acetone and deionized water (each for 15 min), to ensure a clean surface. An alkaline oxidative etchant solution (AOES) was prepared by dissolving $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.913 g) in deionized water (22 mL), followed by dropwise addition of freshly prepared NaOH solution (8 mL, 10 M) with vigorous stirring. After the AOES cooled to room temperature, the copper wire was immersed into the AOES. When the surface of copper wire changed to light blue (~ 15 min), it was withdrawn from the solution, thoroughly rinsed with deionized water and dried in air. Subsequently, the sample underwent 2 h dehydration at 180°C in air with a ramp rate of 2°C min^{-1} , and the color eventually turned to dark brown.

Preparation of the CuO@CoFe-LDH core-shell NWAs

The CuO@CoFe-LDH core-shell NWAs were prepared using a facile electrosynthesis method previously reported by our group [37]. The Cu wire supported CuO NWAs was used as the working electrode in an electrochemical cell with a three-electrode configuration, by using Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte for electrodeposition of CoFe-LDH was obtained by dissolving $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 M) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.15 M) in 50 mL of distilled water. The potentiostatic deposition was carried out at a potential of -1.0 V vs. SCE at room temperature

(25 °C), and the synthesis time ranges in 0–200 s. The resulting Cu wire supported CuO@CoFe-LDH NWAs was withdrawn and rinsed with distilled water. The weight of the active material was obtained by the mass difference between the Cu wire supported CuO@CoFe-LDH NWAs and pure Cu wire substrate.

Preparation of the solid electrolyte

Polyvinyl alcohol (PVA) (molecular weight: 75000–80000) and KOH were used as received. The PVA-KOH solid electrolyte was prepared as follows: PVA (5.0 g) and KOH (5.0 g) were dissolved in 50 mL of water with vigorous and continuous stirring for 5 h at 90 °C, to obtain a complete dissolution and formation of a jelly-like solution. The resulting gel was heated at 60 °C in a vacuum oven to evaporate excess water. The resulting PVA/KOH polymer film was stored in a polyethylene bag before use.

Fabrication of the Cu wire supported active carbon (AC) electrode

The Cu wire supported AC electrode was fabricated by a dip-coating method. Typically, activated carbon (0.6 g), graphene oxide (0.2 g) and acetylene black (0.1 g) were dispersed in 2 mL of ethanol, followed by addition of a polytetrafluoroethylene (PTFE) solution (0.1 g, 20 wt%). The mixture was treated by ultrasonic for 30 min. Subsequently, a Cu wire (0.3 mm in diameter and 12 cm in length) was immersed into the above solution for 10 min, and then was withdrawn and dried by a nitrogen gas flow. The mass-loading of the electrode material was controlled by repeating the above deposition process for several cycles. The obtained Cu wire supported AC electrode was used as the negative electrode for the all-solid-state WSSC.

Fabrication of CuO@CoFe-LDH-based WSSC

The CuO@CoFe-LDH//AC WSSC device was fabricated as follows. Firstly, the positive electrode (Cu wire supported CuO@CoFe-LDH) and the negative electrode (Cu wire supported AC) with the same length were immersed into the PVA/KOH electrolyte for 3 min. After drying at 60 °C for 5 min in vacuum, the two electrodes were taken out and twisted together at about 5 turns per inch in an S twist (left turn). Subsequently, the twisted 2-ply wire was immersed into the PVA/KOH solution for another 15 min. After drying at 60 °C for 24 h in vacuum, the WSSC with a diameter of 0.2 cm and length of 10 cm was obtained.

Characterizations

X-ray diffraction patterns of the core-shell NWAs samples were collected on a Shimadzu XRD-6000 diffractometer using a Cu K α source, with a scan step of 0.02° and a scan range between 3° and 70°. Raman measurements were carried out with 633 nm of excitation by using a confocal Raman microspectrometer (Renishaw, inVia-Reflex, 633 nm). FTIR spectra were recorded on a NICOLET NEXUS470 Fourier transform infrared spectrometer. X-ray

photoelectron spectra (XPS) were performed on a Thermo VG ESCALAB 250 X-ray photoelectron spectrometer at a pressure of about 2×10^{-9} Pa using Al K α X-rays as the excitation source. The morphology of the core-shell NWAs was investigated using a scanning electron microscope (SEM; Zeiss SUPRA 55) with an accelerating voltage of 20 kV, combined with energy dispersive X-ray spectroscopy (EDX) for the determination of metal composition. Transmission electron microscopy (TEM) images were recorded with Philips Tecnai 20 and JEOL JEM-2010 high-resolution transmission electron microscopes. The accelerating voltage was 200 kV in each case.

Electrochemical performance measurements

Electrodes were tested on a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., China) in a three-electrode electrochemical cell using a 1 M KOH aqueous solution as electrolyte at room temperature. The NWAs on Cu wire were directly used as the working electrode. A Pt wire and an Ag/AgCl electrode were used as the counter and reference electrode, respectively. The distance between the working electrode and the counter electrode was 2 cm.

The specific capacitance of the CuO@LDH samples was calculated from the charge-discharge curves based on the following equation:

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (1)$$

where C is the specific capacitance; I (A) refers to the discharge current; ΔV (V) represents the potential change within the discharge time Δt (s), and m corresponds to the total weight of the CuO@LDH NWAs.

The energy density and power density of the flexible WSSC device were calculated using the following equations:

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (2)$$

$$E = \frac{C \times \Delta V^2}{2} \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

where C is the capacitance of the WSSC; I (A) represents the discharge current; ΔV (V) refers to the potential change within the discharge time Δt (s); m is the total volume of the WSSC; E and P correspond to the volumetric energy density and power density, respectively.

Results and discussion

As schematically illustrated in [Scheme 1](#), the copper wire supported hierarchical CuO@CoFe-LDH core-shell NWAs was fabricated by a three-step procedure. Firstly, a fragile copper wire (0.3 mm in diameter) was immersed into an alkaline oxidative etchant solution (AOES) containing (NH₄)₂S₂O₈ and NaOH to produce Cu(OH)₂ NWAs at room temperature for 15 min. Then the obtained Cu(OH)₂ NWAs were heated at 180 °C in air for 2 h to give the well-organized CuO NWAs template. Subsequently, CoFe-LDH nanosheets grow uniformly on the CuO nanowire backbone

by an electrodeposition method, giving rise to the hierarchical CuO@LDH core-shell NWAs supported on Cu wire. SEM images of the as-prepared Cu(OH)₂ NWAs (Figure 1a and b) reveal a high density of NWAs vertically anchoring to the surface of copper wire, with a uniform diameter in the range 190–210 nm and length distribution of 5–6 μm. A further thermal treatment results in the well-organized CuO NWAs with similar morphology to Cu(OH)₂ NWAs precursor (Figure 1c). Finally, after coating with LDH nanoflakes (~150 nm in lateral size and ~12 nm in thickness) by an electrosynthesis route (with an electrosynthesis time of 50 s), core-shell CuO@LDH NWAs with intercrossing CoFe-LDH nanoplatelets shell perpendicularly grafting to the CuO core were obtained (Figure 1d and e). The weight of the active material (CuO@CoFe-LDH NWAs) supported on the copper wire substrate is ~0.08 mg cm⁻¹, and the geographic surface area of the electrode is ~0.0942 cm² cm⁻¹ (diameter: 0.3 mm, close to

the Cu wire substrate). It is found that the electrosynthesis time (0–200 s) of LDH shell imposes a significant influence on the shell thickness and morphology (Figure S1): a prolonged time leads to a thicker and denser LDH shell. The core-shell nanostructure is further confirmed by TEM (Figure 1f), from which the core diameter of ~205 nm and shell thickness of ~146 nm are identified clearly. The *d*-spacing from high resolution TEM (HRTEM) is ~0.25 nm, corresponding to the LDH (0 1 2) plane [35], as indicated by the lattice fringes (Figure 1f, inset). EDX results with a line scanning (Figure 1g and h) and mapping analysis (Figure 1i) show that copper is located in the central part of the NWs while both cobalt and iron are homogeneously distributed throughout the whole NWs. In addition, elemental contents of Cu, Co, Fe and O of CuO@LDH NWs are 18.16 %, 16.95 %, 8.62 % and 56.28 %, respectively, which are measured by EDX spectra (Figure S2).

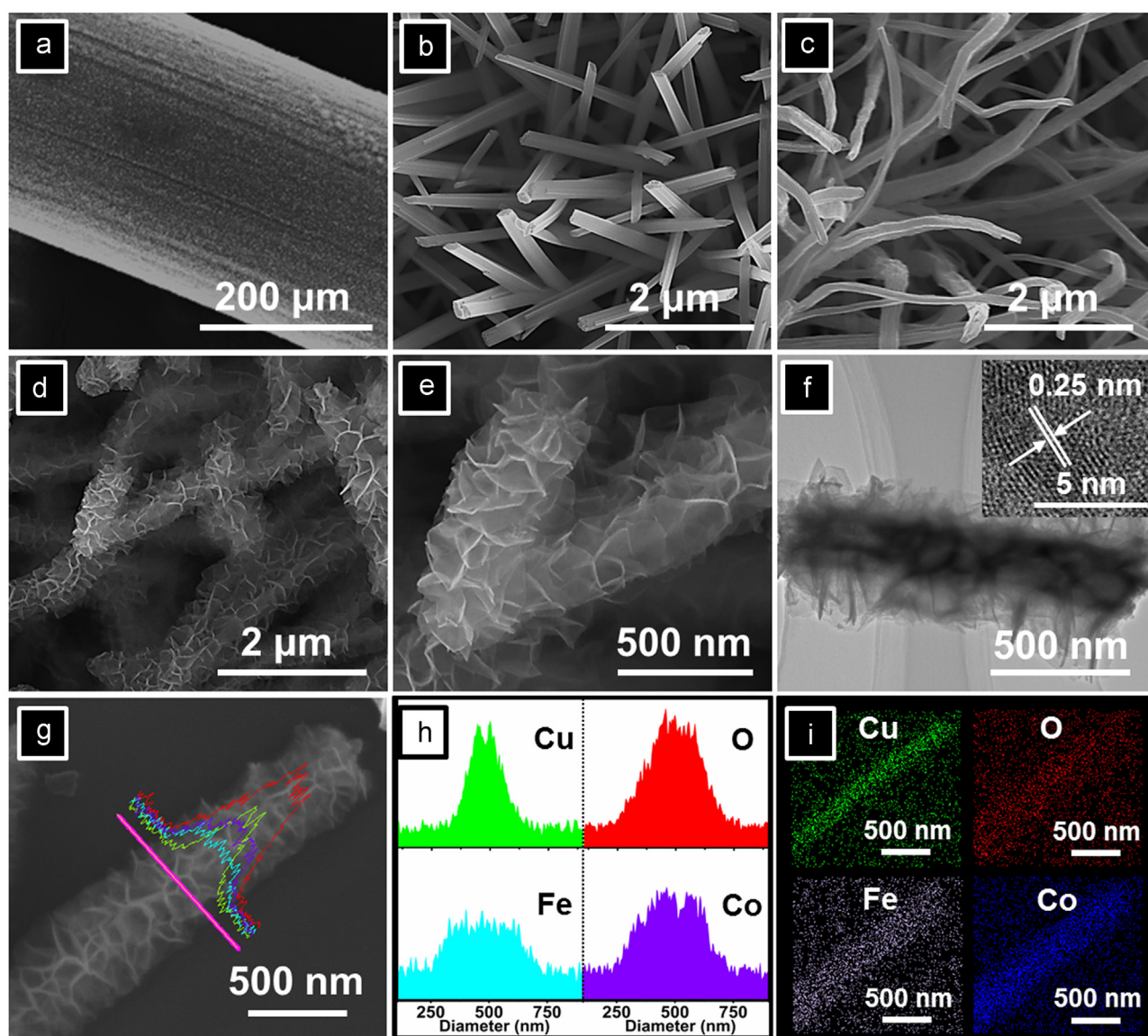


Figure 1 SEM images of (a, b) the copper wire coated with Cu(OH)₂ NWAs, (c) CuO NWAs and (d, e) CuO@CoFe-LDH NWAs. (f) TEM image of CuO@CoFe-LDH NWAs (inset: the corresponding HRTEM image). (g, h) Line scan results and (i) EDX mapping of CuO@CoFe-LDH NWAs.

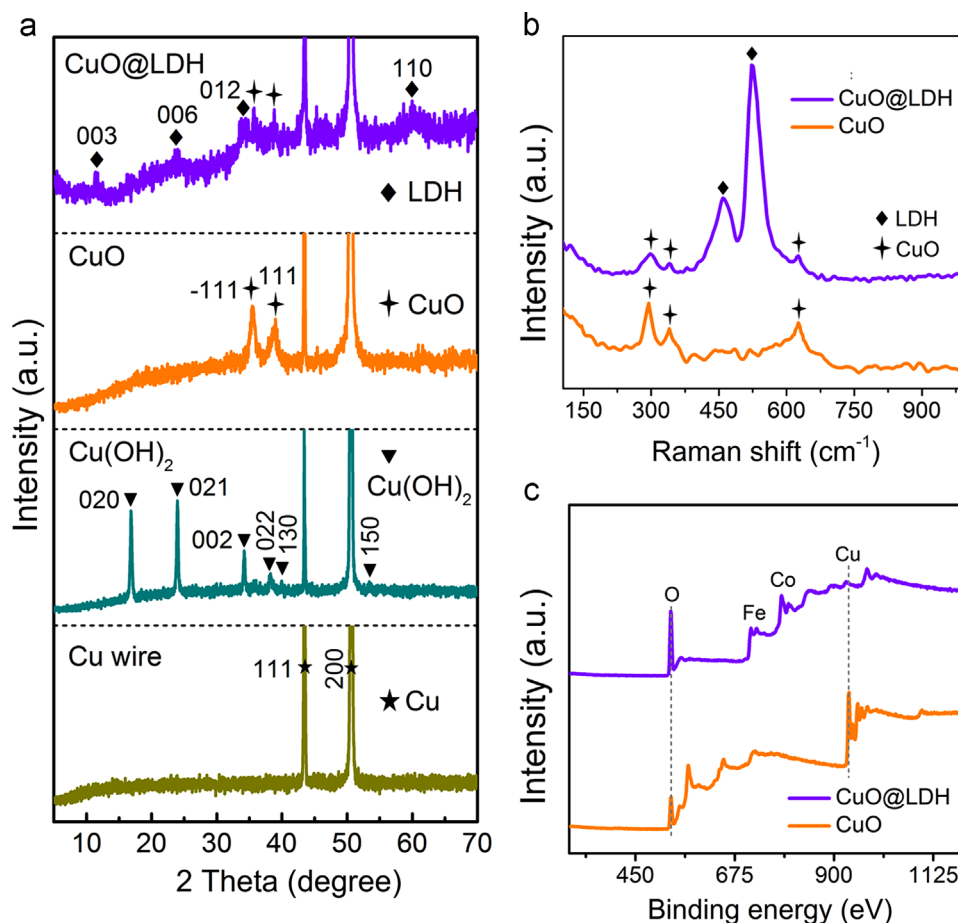


Figure 2 (a) XRD patterns of Cu wire substrate, Cu(OH)₂ NWAs, CuO NWAs and CuO@CoFe-LDH NWAs, respectively. (b) Raman and (c) XPS spectra for the pristine CuO and CuO@CoFe-LDH NWAs, respectively.

Figure 2a show the XRD patterns of Cu wire substrate, Cu(OH)₂ NWAs, CuO NWAs and CuO@CoFe-LDH NWAs, respectively. The Cu wire shows two strong reflections (2θ 43.3° and 50.4°) indexed to the (111) and (200) plane of a cubic metallic copper. For the Cu(OH)₂ NWAs, diffraction peaks at 2θ 16.6°, 23.7°, 34°, 35.8°, 38.1°, 39.7° and 53.3° are clearly identified, corresponding to the (020), (021), (002), (111), (022), (130), and (150) plane of an orthorhombic Cu(OH)₂. After heat treatment, the original peaks are replaced by two neonatal ones at 35.5° and 38.8°, which are assigned to the (-111) and (111) planes of a monoclinic CuO [36]. After coating with the LDH shell, the XRD pattern of the resulting material displays a superimposition of a CuO phase and LDH phase. The (003), (006), (012) and (110) reflection at 2θ 11.7°, 23.5°, 34.8° and 59.7° for a typical LDH material are observed, indicating a high crystallinity [35]. The chemical composition and structure of CuO@CoFe-LDH core-shell NWAs are further studied by Raman spectra, FT-IR, and XPS technique. Raman spectrum of CuO@CoFe-LDH (Figure 2b) shows three peaks at 295.1, 342.5 and 633.8 cm⁻¹, corresponding to the A_g (296 cm⁻¹), B_g⁽¹⁾ (346 cm⁻¹), and B_g⁽²⁾ (636 cm⁻¹) mode of CuO backbone, respectively [38]; the peak at 456 cm⁻¹ and 523 cm⁻¹ are attributed to the stretching of OH-O bond between carbonate ion and water molecule in the interlayer region of CoFe-LDH [28]. FT-IR spectrum of CuO@CoFe-LDH NWAs (Figure S3) displays a new band at 1468 cm⁻¹ compared

with the CuO substrate, which is assigned to the ν_3 mode of interlayer carbonate species for LDH [35]. Moreover, surface elemental analysis was carried out by XPS over the CuO and CuO@CoFe-LDH NWAs sample. The full XPS spectrum of CuO@CoFe-LDH NWAs reveals signals of Cu, Co, Fe, O and C element; while Co and Fe 2p peak is absent in pristine CuO NWAs (Figure 2c). Figure S4 further shows the Co 2p, Fe 2p and Cu 2p core level spectra of the as-synthesized CuO@CoFe-LDH NWAs sample. The Co 2p_{3/2} spectrum displays a complex structure broadened by multiplet splitting effect (Figure S4a), whose binding energy can be decomposed to 782.3 and 780.1 eV, indicating the presence of both Co²⁺ and Co³⁺ oxidation state in the CuO@CoFe-LDH sample [39]. The binding energies of Fe 2p_{3/2} (711.0 eV) and Fe 2p_{1/2} (724.9 eV) are observed (Figure S4b), corresponding to the Fe(III) oxidation state [37]. In the case of Cu 2p (Figure S4c), the binding energies of Cu 2p_{3/2} and Cu 2p_{1/2} are respectively located at 934.5 and 954.9 eV for pristine CuO NWAs sample, with a spin energy separation of 20.4 eV, in good agreement with the reported data of Cu 2p state in CuO NWAs [40]. After the electrodeposition of CoFe-LDH shell, both the Cu 2p_{3/2} and Cu 2p_{1/2} peak shift to a higher energy level (934.8 and 955.2 eV, respectively), along with a sharp decrease in the intensity, suggesting an interaction between CuO core and CoFe-LDH shell.

The electrochemical tests were performed in a three-electrode cell at room temperature with a Pt wire counter

electrode and an Ag/AgCl reference electrode in 1.0 M KOH aqueous electrolyte (Figure 3a). Figure 3b shows the cyclic voltammograms (CVs) of pristine CuO NWAs, CoFe-LDH nanoarrays (NAs; Figure S5), and CuO@CoFe-LDH NWAs (with an electrosynthesis time of 50 s) at a scan rate of 50 mV s^{-1} . For CuO NWAs, the reduction peaks at 0.35 V and 0.21 V are attributed to the conversion of Cu(III) to Cu(II) and Cu(II) to Cu(I), respectively (orange curve in Figure 3b) [41]. In contrast, the pristine CoFe-LDH NAs sample consists of two pairs of redox peaks at ~ 0.25 and ~ 0.35 V (dark cyan curve in Figure 3b), corresponding to $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Co}^{3+}/\text{Co}^{4+}$ associated with OH^- , respectively [39]. In the case of CuO@CoFe-LDH NWAs sample (violet curve in Figure 3b), the integral area of CV curve increases obviously, indicating a largely enhanced capacitance. Figure 3c shows the galvanostatic (GV) charge/discharge characteristics of CuO NWAs, CoFe-LDH NAs, and CuO@CoFe-LDH NWAs (current density: 2.5 mA cm^{-2} ; potential range: 0–0.45 V), respectively. The charge/discharge characteristics of all these samples exhibit a typical pseudo-capacitive behavior, consistent with the results of CVs. The corresponding specific capacitance are calculated to be 694, 755, and 866 mF cm^{-2} for the CuO NWAs, CoFe-LDH NAs, and CuO@CoFe-LDH NWAs,

respectively, demonstrating the highest specific capacitance for the CuO@CoFe-LDH sample. It is worth mention that the electrosynthesis time of LDH shell imposes a significant influence on the supercapacitive performances of CuO@CoFe-LDH samples. The specific capacitance for the core-shell electrode increases along with the elongated deposition time of LDH and reaches a maximum for the CuO@CoFe-LDH-50 s (866 mF cm^{-2}), indicating a largely enhanced capacitance. However, the capacitance decreases to 792 mF cm^{-2} for CuO@CoFe-LDH-100 s, which demonstrates that an excess of LDH incorporation leads to a depressed electrochemical activity (Figure S6). This can be explained that an over-dense packing of LDH shell on CuO core gives less exposure of active sites, which thereby diminishes the faradic reactions and hinders the charge transfer.

Rate capability is a key factor for evaluating the power applications of supercapacitors, which is determined by using the GV technique at different charge/discharge current densities (Figure S7). The specific capacitances of the three samples derived from the discharging curves at various charge/discharge current densities are shown in Figure 3d. Within the whole current density range, the CuO@CoFe-LDH yields a substantially higher specific

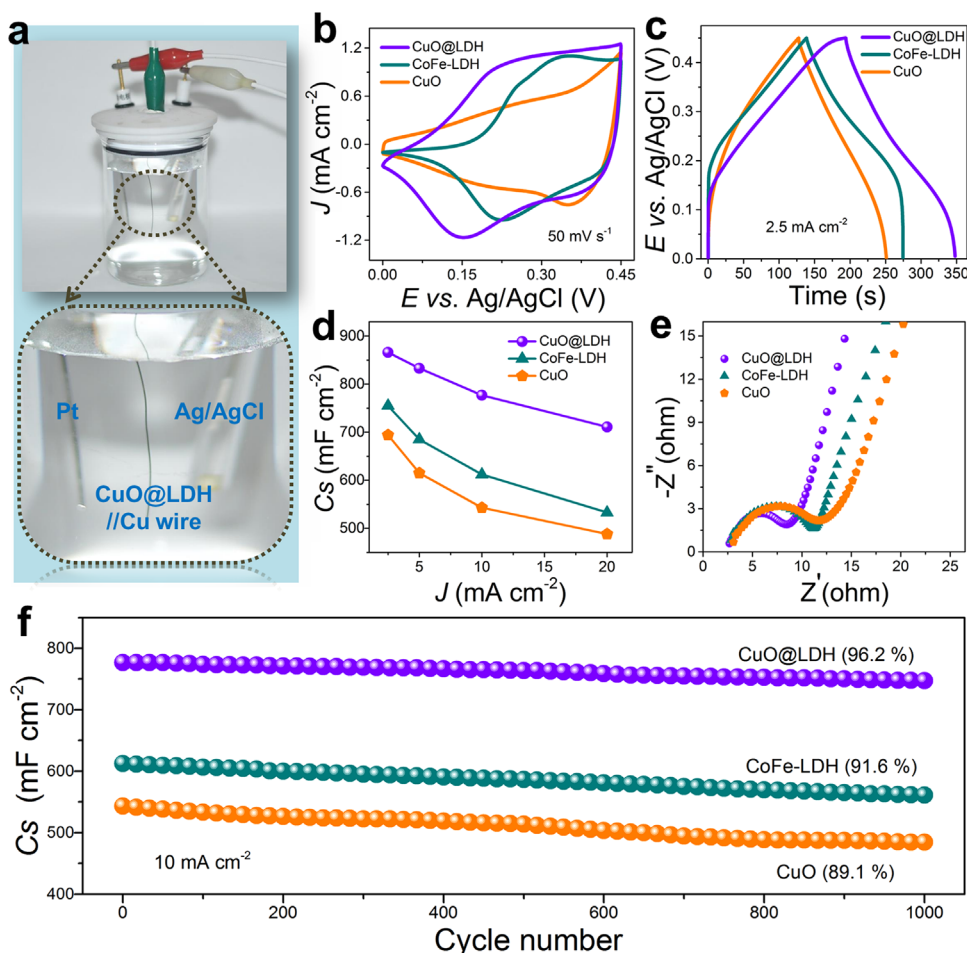


Figure 3 (a) Photographs of the three-electrode electrochemical cell. (b) Cyclic voltammetry (CV) curves, (c) galvanostatic (GV) charge/discharge curves and (d) current density dependence of the specific capacitance for the pristine CuO, CoFe-LDH, and CuO@CoFe-LDH sample. (e) Nyquist plots of EIS and (f) cycling performance for the pristine CuO, CoFe-LDH, and CuO@CoFe-LDH sample.

capacitance than that of the other two samples. At a high current density of 20 mA cm^{-2} , the specific capacitance of pristine CuO NWAs and CoFe-LDH sample maintains 69.5% and 70.6%, respectively. In the case of CuO@CoFe-LDH sample however, 82.1% of the capacitance is still retained. The enhanced electrochemical performance of CuO@CoFe-LDH NWAs was further confirmed by the electrochemical impedance spectroscopy (EIS) measurements. Figure 3e shows the Nyquist plots of EIS spectra for CuO NWAs, CoFe-LDH NAs, and CuO@CoFe-LDH NWAs. All of the curves consist of a semicircle in high frequency region and a straight line in low frequency region. The semicircle diameter reflects the charge transfer resistance, while the slope of straight line indicates the ion diffusion resistance

[42]. The CuO@LDH NWAs exhibit a smaller semicircle diameter and larger slope than those of CuO NWAs and CoFe-LDH NAs, which indicates a faster electron transport kinetics and ion diffusion rate at the electrode/electrolyte interface. It is reported that the redox reaction of LDHs involves the reversible uptake and release of OH^- from the solution associated with electron transfer from/to the current collector [39,43]. The hierarchical structure of LDH shell facilitates the effective exposure of surface active sites for this Faradic redox reaction and thus benefits the interfacial charge transportation process. Cycling capability is an important requirement for supercapacitor applications, which was carried out over CuO@CoFe-LDH electrode for 1000 cycles by using GV charge/discharge technique

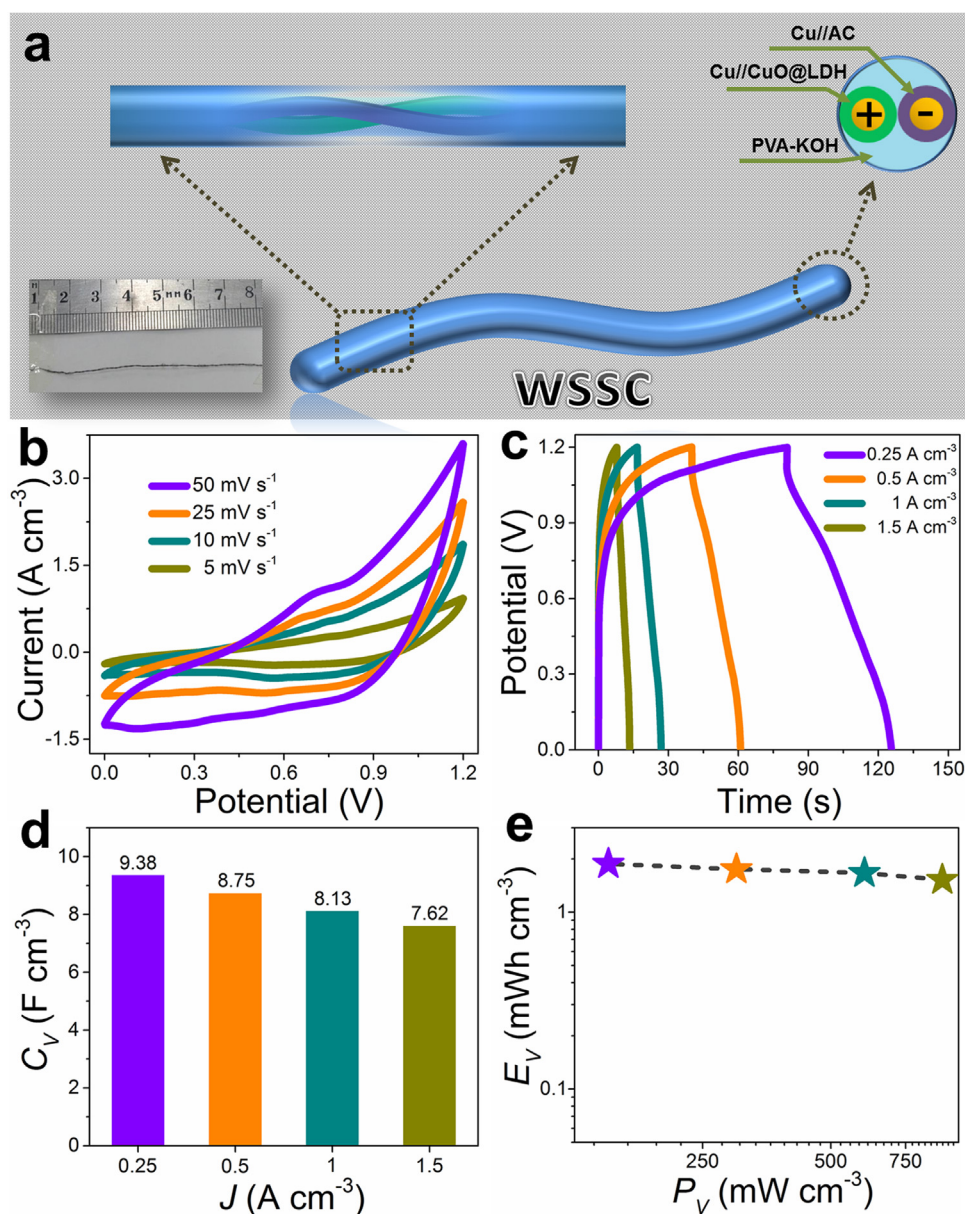


Figure 4 (a) Schematic representation of the flexible asymmetric wire shaped all-solid-state supercapacitor based on CuO@CoFe-LDH, active carbon electrode, and PVA/KOH electrolyte (the inset shows the photograph of the as-prepared WSSC). (b) CV curves, (c) GV charge/discharge curves and (d) current density dependence of the specific capacitance for the wire-shaped device at various scan rates. (e) Ragone plots of the WSSC.

(Figure 3f; current density: 10 mA cm^{-2} ; potential window: 0–0.45 V). The specific capacitance of CuO@CoFe-LDH maintains 96.2% after 1000 cycles, much superior to the pristine CuO (89.1% retention) and CoFe-LDH sample (91.6% retention). The long-term electrochemical stability of CuO@CoFe-LDH electrode is demonstrated by the very stable charge/discharge curves for the last 20 cycles (Figure S8).

WSSCs are promising for the next generation of micro-electronic devices owing to their merits of tiny volume, high flexibility and wearability. In order to demonstrate the potential of CuO@CoFe-LDH grafted on copper wire electrode for the WSSC application, a wire-shaped asymmetric all-solid-state micro-supercapacitor was fabricated by using

CuO@LDH NWAs as the positive electrode, a Cu wire supported active carbon (AC) as the negative electrode and poly(vinyl alcohol) (PVA)/KOH as the solid electrolyte. As for the negative electrode, numerous interconnected active carbon nanoparticles are uniformly coated on the surface of Cu wire, and the diameter of the whole negative electrode is $\sim 0.35 \text{ mm}$ (Figure S9). The configuration of the all-solid-state flexible WSSC described herein is schematically shown in Figure 4a. Its SEM image reveals that the two intertwined electrodes are fully surrounded by the PVA/KOH solid electrolyte (Figure S10), which guarantees necessary medium conditions toward redox reactions. The whole surface area of the fabricated WSSCs is 6.28 cm^2 and the volume of the whole cell is 0.314 cm^3 . Figure 4b displays the

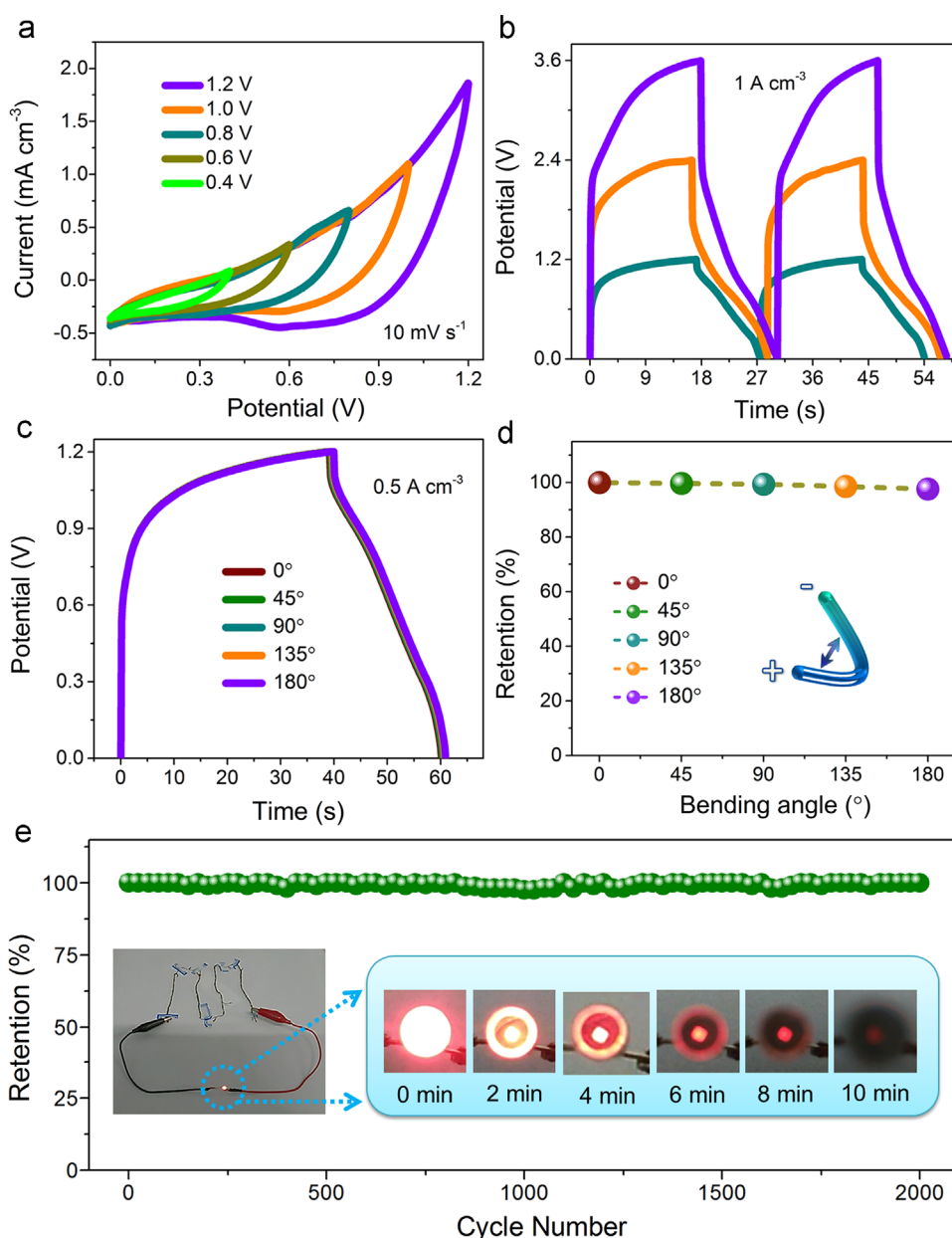


Figure 5 (a) CV curves of the asymmetric supercapacitor with the increase of potential window. (b) GV charge/discharge curves for the WSSC in series. (c) galvanostatic charge/discharge curves and (d) the corresponding capacitance retention of the WSSC bending at different angles. (e) Cycling performance of the wire-shaped device at a current density of 0.5 A cm^{-3} for 2000 cycles (inset: four single WSSC unit connected in series to light a red light-emitting-diode).

CV curves of the asymmetric WSSC measured at the scan rate $5-50 \text{ mV s}^{-1}$ between 0 and 1.2 V. The obtained fiber-shaped all-solid-state device exhibits a pair of redox peaks, indicating a typical pseudo-capacitive behavior. The specific capacitance of the WSSC as a function of current density is further calculated based on the galvanostatic charge-discharge curves (Figure 4c and d), from which a retention of 81.2% is obtained (from 9.38 F cm^{-3} at 0.25 A cm^{-3} to 7.62 F cm^{-3} at 1.5 A cm^{-3}). The energy and power density, resulting from GV curves and plotted on the Ragone diagram (Figure 4e), further evaluate the energy efficiency of this wire-shaped device. Impressively, a maximum energy density of $93.75 \text{ } \mu\text{Wh cm}^{-2}$ ($1.857 \text{ mWh cm}^{-3}$) and power density of $45720 \text{ } \mu\text{W cm}^{-2}$ (914.5 mW cm^{-3}) are achieved at an operating voltage of 1.2 V, superior to previously reported WSSCs systems such as RGO//CNT@CMC YSCs [44], ZnO nanowires//MnO₂ [9] and Co₃S₈ nanorod//Co₃O₄@RuO₂ [45] (see Table S1 for the detailed comparison).

From the viewpoint of practical applications, soft and portable electronics require highly flexible power sources working at various operation voltages and powers. Figure 5a shows a series of CV measurements of the wire shaped asymmetric devices at different cell voltages varying from 0.0-0.4 V to 0.0-1.2 V. It is observed that the Faradic reaction occurs more sufficiently (the larger integrated CV area) with the increase of operating potential to 1.2 V. Moreover, we further made serial connection to control over the operating voltage and current. Within the same discharge time, the operating voltage can be elevated from 1.2 V for a single WSSC to 2.4 V and 3.6 V by connecting two and three WSSCs in series, respectively (Figure 5b). The effect of curvature on this CuO@CoFe-LDH-based WSSC performance was examined by testing the galvanostatic charge/discharge behavior at five different bending angles (from 0° to 180°). As shown in Figure 5c, no apparent change in the charge/discharge curves is observed ($\sim 93.5\%$ capacitance is maintained with a bending angle of 180° based on the discharge curves; Figure 5d), revealing a satisfactory electrochemical performance of the WSSC even under the bending conditions. Furthermore, Figure 5e displays the long-term cycle stability by GV charge/discharge at a current density of 0.5 A cm^{-3} , which shows a capacitance retention of 99.5% over 2000 cycles. To further test this asymmetric WSSC, four single units are connected in series to light a red light-emitting-diode (Figure 5e, inset) for 10 min, demonstrating its suitability as a flexible micro energy storage device for practical applications.

Conclusion

In summary, well-aligned CuO@CoFe-LDH core-shell NWAs have been successfully synthesized by the electrodeposition of CoFe-LDH nanoplatelets on the surface of CuO nanowires. Benefiting from the hierarchical core-shell nanostructure and the efficient pseudocapacitance properties of CuO and CoFe-LDH, the as-fabricated asymmetrical all-solid-state WSSC device exhibits a high energy density ($1.857 \text{ mWh cm}^{-3}$ for volumetric energy density) and excellent cycling stability (99.5% device capacitance retention over 2000 cycles). By virtue of the versatility of metal wire substrates, transition metal oxides and LDHs, the synthesis strategy

presented here can be extended to the fabrication of other portable and flexible micro energy storage devices.

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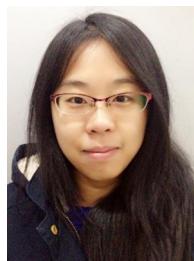
Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2015.12.030>.

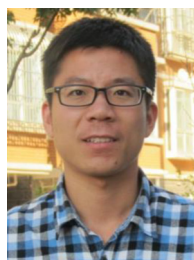
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Lei Zhou received her Bachelor's degree in 2013 from Beijing University of Chemical Technology. She joined Professor Xue Duan's group as a PhD candidate at Beijing University of Chemical Technology in 2013. His research interests currently focus on the design and fabrication of electrodes for small molecules electrocatalysis.



Ruikang Zhang received his Bachelor's degree in 2012 from East China University of Science and Technology. He joined Professor Xue Duan's group as a PhD candidate at Beijing University of Chemical Technology in 2013. His research interests currently focus on the design and fabrication of photoelectrodes for water splitting.



Cong Zhang received her Bachelor's degree in 2012 from Yanching Institute of Technology. She is now a Ph.D. candidate under the supervision of Prof. Min Wei in the Beijing University of Chemical Technology (BUCT). Her research interests mainly focus on design and fabrication of oxygen evolution reaction (OER) electrode for electrochemical water splitting.



Jingbin Han received his PhD degree from Beijing University of Chemical Technology (BUCT) in 2011 under the supervision of Prof. Xue Duan, after which he continued working as a staff in BUCT. He has been a visiting student and visiting scholar in the Georgia Institute of Technology (in 2008) and the University of Oxford (in 2014), respectively. His research interests focus on the design and fabrication of organic-inorganic hybrid materials with new functionality, including energy storage and gas barrier properties.



Zhenhua Li received his Bachelor's degree from Beijing University of Chemical Technology (BUCT) in Polymer Science and engineering in 2014. He is now a post-graduate under the supervision of Prof. Xue Duan in the BUCT. His research interests mainly focus on the synthesis of nanostructured layered double hydroxides and their application in the energy storage and conversion.



Mingfei Shao received his PhD degree from Beijing University of Chemical Technology in 2014 supervised by Prof. Xue Duan, after which he joined the staff of BUCT. He has been a visiting student in the University of Oxford (in 2013). His current research interests are mainly focused on the controlled synthesis of layered functional materials and their applications in electrochemical and photoelectrochemical energy storage

and conversions.



Min Wei obtained her BEng degree in 1995 and MEng degree in 1998 from Beijing University of Chemical Technology (BUCT). She subsequently received her PhD from Peking University in 2001, after which she joined the staff of BUCT. She was promoted to full Professor in 2005. She has been a visiting scholar in the Georgia Institute of Technology (in 2008). Her research interests focus on inorganic-organic composite functional materials as well as new catalysts.



David G. Evans studied as both an undergraduate and a research student at Jesus College, Oxford, and obtained a DPhil under the supervision of Prof. D. M. P. Mingos FRS. After postdoctoral work at Bristol University with Prof. F. G. A. Stone FRS, he was appointed as a lecturer at Exeter University in 1985. Several visits to Chinese university chemistry departments in the early 1990s convinced him of China's great potential for development and he moved to Beijing University of Chemical Technology in 1996. His research interests focus on intercalation in layered solids.



Xue Duan was elected as an Academician of the Chinese Academy of Sciences in 2007. He was awarded his BS degree from Jilin University and MS and PhD degrees from Beijing University of Chemical Technology (BUCT). He was subsequently appointed to the staff of BUCT and established the Applied Chemistry Research Institute in 1990. He was promoted to full Professor in 1993 and to PhD supervisor status in 1995.

He is currently Director of the Institute of Applied Chemistry and Executive Vice-Chair of the Academic Committee of the State Key Laboratory of Chemical Resource Engineering.