Design and Construction of Three-Dimensional CuO/Polyaniline/rGO Ternary Hierarchical Architectures for High Performance Supercapacitors

Sheng Zhu^a, Mi Wu^a, Mei-Hong Ge^a, Hui Zhang^a, Shi-Kuo Li^{a*}, Chuan-Hao Li^{b*}

^aLab of Clean Energy & Environmental Catalysis, School of Chemistry and Chemical Engineering, School of Physics and Materials Science, Anhui University, Hefei 230601, P. R. China

^bDepartment of Chemical & Environmental Engineering, Yale University, New Haven, US 06511

GRAPHICAL ABSTRACT

ABSTRACT

Rational design in terms of component and microstructure and fabrication of electrochemical electrodes are crucially important towards superior energy storage device. Herein, we report a novel CuO-PANI-rGO ternary hybrid electrode self-assembled by an in situ polymerization method combined with hydrothermal route for electrochemical capacitor. Well-defined CuO hierarchical architecture is synthesized by the spontaneous oxidization of Cu nanowire. PANI acts as not only binder for anchoring CuO architecture on rGO surface, but also charge transport channels, and high specific capacitance donor to the whole electrode matrix. The typical CuO-PANI-rGO ternary hybrid electrode can be reversibly cycled in a high voltage region up to 1.2 V. And it displays a maximum specific capacitance of 634.4 F g⁻¹ and a high energy density of 126.8 Wh kg⁻¹ with a power density of 114.2 kW kg⁻¹ at a current density of 1.0 A g⁻¹. Furthermore, the ternary hybrid electrode exhibits great cycle life with 97.4% specific capacitance retention after 10000 cycles. Those excellent performances are proposed to derive from the well-defined

*Corresponding author. Tel.: +86-551-63861328.
E-mail: lishikuo@ahu.edu.cn (S. Li), chuanhao.li@yale.edu (C. Li).

nanostructure, conductive porous microstructure and homogenously contact. This study might be important for designing the unique structure and component electrode for achieving high performance energy storage device.

5 **Keywords:** CuO hierarchical architecture; PANI; Self-assembly; High energy density; Supercapacitor.

1. Introduction

Electrochemical capacitor (also named supercapacitor) has been recognized as one of the most
10 attractive next-generation energy storage devices due to its high power density, long cycle life, rapid charge/discharge rate and low maintenance cost [1-3]. However, the energy density (<10.0 Wh kg^{-1}) of the devices is much lower than that of a lithium secondary battery (~ 200.0 Wh kg^{-1}) [4], which seriously hinder its widespread applications. Enlarging the cell voltage and/or specific capacitance is thought to be an effective way to get high energy density for supercapacitors. In
15 general, high surface area and excellent electrical conductivity are strongly beneficial for achieving high energy density for the hybrid pseudo-capacitance electrodes with carbonaceous materials including activated carbon [5, 6], carbon nanotubes or nanofibres [7-9], graphene [10-13], and conducting polymers [14, 15]. The porous hybrid carbonaceous electrodes can not only enhance the specific capacitance and cycle ability, but also contribute large electrolyte-electrode
20 interface for charge smooth diffusion. As the most promising carbon materials, the monolayer graphene is important for constructing three-dimensional hierarchical architectures through the self-aggregation reaction in high temperature. It has been extensively investigated as excellent building blocks for developing porous energy storage devices.

Copper oxide (CuO) is an earth-abundant and relatively inexpensive metal oxide. It has
25 attracted much research interest as a promising electrochemical electrode [16-18]. The redox reactions involved in the charge/discharge process can be conveniently transformed between Cu (II) and Cu (I) species. Several different types of CuO nanostructures such as nanosheet [17, 19], nanowire [16], lotus-like [20], flower-like [21, 22], core-shell nanostructure [18] and the formation of nanocomposite [23, 24] have been investigated for their excellent electrochemical
30 performances. In comparison, linear hierarchical architecture would be specially beneficial for electrochemical electrode due to its larger surface area and shorter diffusion lengths for electrons and cations [25, 26]. However, the poor electrical conductivity, low mechanical stability, and rapid capacity decay largely hinder its further applications. Graphene is regarded as a suitable substrate to enhance the conductivity and stability of CuO nanostructures. Incorporation of well-defined

CuO architecture with **graphene oxide (GO)** into porous frameworks has been considered as an effective way to improve their electrochemical properties. The hybrid materials prepared by *in situ* deposition protocols usually exhibit unsatisfied electrochemical performances because of the difficulty in morphology and mass-loading control for the pseudo-capacitance materials [27-29].

5 The porous framework with high surface area and abundant conductive pore network can increase the electrode–electrolyte interfacial contact and alleviate the diffusion resistance during charge/discharge process [30, 31]. Very recently, we assembled an interconnected rGO/ β -MnO₂ binary hybrid electrode with ultrafine MnO₂ nanostructure and precisely mass-loading control for high performance supercapacitor [32]. The electrochemical properties of porous composites are
10 mainly dependent on the contact and dispersion of the nanomaterials with the carbonaceous substrates. Therefore, it is highly desired to prepare porous hybrid composites with well-defined nanostructures, precise mass-loading control, and homogenous contact for improving their energy storage capacity.

In this work, we designed a CuO hierarchical architecture anchored polyaniline (PANI)/reduced
15 graphene oxide (rGO) ternary hybrid electrode by *in situ* polymerization method combined with hydrothermal route as high energy density supercapacitor. The fabrication process of the ternary hybrid electrode is shown in Scheme 1. Well-defined CuO hierarchical architecture is obtained by the spontaneous oxidization of the active Cu nanowires (NWs) at ambient temperature, which is attached on GO surface with the assistance of PANI. The presence of PANI plays a couple of roles
20 including: (1) anchoring CuO hierarchical architecture on rGO surface for homogeneously interfacial contact, (2) enhancing the conductivity and active sites for electron transportation and ion diffusion within the ternary hybrid sample, and (3) providing high specific capacitance for the ternary hybrid sample. The electrochemical performances of the ternary hybrid samples are greatly enhanced by its unique structure and the synergistic effect of the ternary components compared
25 with the pure rGO sample, rGO/CuO and PANI-rGO binary hybrid samples. The maximum specific capacitance of the typical CuO-PANI-rGO ternary hybrid electrode is 634.4 F g⁻¹ with a high energy density of 126.8 Wh kg⁻¹ and a power density of 114.2 kW kg⁻¹ in 1.0 M Na₂SO₄ aqueous solution at current density of 1.0 A g⁻¹. Furthermore, the stability tests indicate that the typical ternary hybrid device could maintain 97.4% specific capacitance after 10000 cycles.
30 Besides, two CuO-PANI-rGO electrodes are connected in series to fabricate a real device. After charging for only 10 s at a current density of 25.0 A g⁻¹, the device could power 33 red light-emitting diode (LED) lamps for about 15 min, suggesting the ternary hybrid electrode a promising candidate as high performance energy storage device.

2. Experimental Section

2.1. Synthesis of hierarchical Cu@CuO linear heterostructure with uniform morphology

The hierarchical Cu@CuO linear heterostructure was synthesized according to spontaneous oxidization of the active Cu NWs under ambient temperature. Firstly, Cu NWs were obtained according to a reported method [33]. The precursor solution was prepared by mixing 10.0 mL 1.0 mM trihydrate copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) with 250.0 mL 15.0 M chilled (at 10 °C) sodium hydroxide (NaOH) solution in a 500 mL round-bottom flask. Then, 2.25 mL ethylene diamine (EDA), 0.10 mL 85.0 wt% hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) was injected into the flask, respectively. Following each addition step, the flask was capped and shaken for about 10 min to distribute the reactants. The sealed flask was then placed in a 60 °C water bath for 1 h under magnetic stirring. The color of the mixed solution gradually changed to red, indicating the reactions occurred at that condition as shown in Fig. S3 (see Supporting Information). Subsequently, the flask was cooled in an ice bath until the solution temperature dropped to 10 °C. Finally, the product was collected by filtering and washing with excess water for several times to removal any impurities. Prior to drying, the filter cake was preserved in an argon environment. Secondly, the hierarchical Cu@CuO linear heterostructure with uniform morphology was synthesized by the epitaxial growth of the as-prepared Cu NWs in aqueous solution via a spontaneous oxidization process in ambient temperature for 12 h without any helps of additives.

2.2. Self-assembly of the hierarchical CuO-PANI-rGO ternary hybrid hydrogel

In a typical self-assembly procedure, 0.2 mL aniline was first injected into 10.0 mL 0.2 g mL⁻¹ GO suspension under ultrasonication [34]. Then, the mixed concentrated hydrochloric acid (HCl) and ammonium persulfate (APS) aqueous solution (10.0 mL) was slowly added to the above suspension under vigorous stirring. The molar ratio of aniline, HCl and APS was adjusted to 1:1:1. To study the effect of PANI to the electrochemical performances of the ternary hybrid sample, the feeding weight ratio of aniline to GO was changed as 1:100, 2:100, and 4:100. After the reaction was performed in ice bath for 10 minutes, 9.0 mL 1.0 M HCl together with 0.2 mL aniline was added to the reaction system, following by addition of different amounts of the as-synthesized. The suspensions were stirred for 12 h to disperse the reactants. Subsequently, the green mixtures were sealed in 25 mL Teflon-lined stainless steel autoclaves and maintained at 180 °C for 12 h. After reaction, the autoclaves were allowed to naturally cool to room temperature and the hierarchical CuO-PANI-rGO ternary hybrid hydrogels were obtained and collected with tweezers, which were freeze-dried under vacuum for further characterization. For comparison, only Cu@CuO linear heterostructure, rGO hydrogel, CuO-rGO and PANI-rGO binary hybrid hydrogels were also fabricated by the same hydrothermal process.

2.3. Characterization

The sample morphology and structure were characterized using scanning electron microscopy (SEM, JSM-7000), transmission electron microscopy (TEM, JEOL 2100), and X-ray diffraction spectroscopy (XRD, Philips X'Pert PRO SUPER). Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a FTIR system (NEXUS-870) with KBr pellets. Raman spectra were recorded using a confocal Raman Spectrometer (LabRAM HR) with a 532 nm laser. Brunauer–Emmett–Teller (BET) specific surface areas were measured through nitrogen sorption isotherms that were acquired from a V-Sorb2800P analyzer at 77 K. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALab MKII spectrometer with Al K α (1486.6 eV) as the X-ray source. All of the data acquisition and processing were accomplished on XPS PEAK software. Thermogravimetric (TG) analysis was conducted on a TG Q2000 analyzer from 20 to 800 °C under air with a heating rate of 10 °C min⁻¹.

2.4. Electrochemical Measurements

The hierarchical CuO-PANI-rGO ternary hybrid hydrogels were directly used as working electrodes without any ancillary materials. Two slices of CuO-PANI-rGO ternary hybrid hydrogels with a thickness of about 1 mm were first carefully cut from the cylindrical sample, which were then immersed in 1.0 M Na₂SO₄ aqueous electrolyte overnight to fully exchange their interior water with the electrolyte [35]. Then the slices were fabricated on Pt foils (2.0×3.0 cm) and separated by a filter paper soaked with electrolyte solution (1.0 M Na₂SO₄). In these experiments, Pt foils were used as the current collectors. The loading mass of the active material on Pt foils was about 1.0–2.0 mg. **The mass ratio of anode and cathode is fixed at 1:1 for the present symmetric electrodes.** The materials were assembled into a layered and sandwiched structure between two polytetrafluoroethylene sheets with parafilm. As for CuO-PANI-rGO ternary mixed electrode, 15 wt% acetylene black and 5 wt% polyvinylidene fluoride in ethylene solution were added to as-prepared composites to form a homogeneous paste and then pressed into Pt foils current collectors. The as-prepared electrode was then dried under vacuum at 60 °C for 12 h. CV, GCD, and EIS measurements were carried out on CHI 660E electrochemical workstation with two-electrode system at room temperature. The voltage range for CV and GCD tests was 0–1.4 V. EIS tests were carried out in the frequency range of 10⁵–0.01 Hz.

3. Results and Discussion

Spontaneous oxidization reaction of the active Cu NWs at ambient temperature was utilized to synthesize the hierarchical Cu@CuO linear heterostructure. The reaction between Cu NWs and the dissolved oxygen in aqueous solution can be described as shown in Fig. S1 (see Supporting Information). The advantage of this epitaxial growth process is that hierarchical CuO coating can be uniformly formed on the surface of Cu NWs, which can efficiently hinder the adjacent

nanosheet aggregation. As shown by the X-ray diffraction (XRD) pattern in Fig. S2 (see Supporting Information), two apparent new reflection peaks appeared at 35.4° and 38.6° after the oxidization of Cu NWs, which can be indexed to the $(\bar{1}11)$ and (111) plane of monoclinic CuO crystalline structure (JCPDS card No. 80-1916). There are no characteristic peaks of impurities, such as $\text{Cu}(\text{OH})_2$ or Cu_2O , indicating that CuO phase is finally obtained on the surface of Cu NWs by its spontaneous oxidization. The schematic structure of the sample is presented as an inset in Fig. S2. As can be seen, Cu atoms are interacted with O atoms in the surface of Cu NWs during the oxidization process. The morphology and crystalline structure of the hierarchical Cu@CuO linear heterostructure was further characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. As shown in Fig. 1a, the product is composed of uniform linear hierarchical architecture in a large scale. The average diameter is in the range of 220–280 nm, and the length can reach tens of micrometers. From the high magnification SEM image (Fig. 1b), it can be observed that the nanosheets are uniformly grown on the linear core with a conformal coating. It exhibits a hierarchical array feature with enough space among the adjacent nanosheets. Such character could facilitate the penetration of the electrolyte, which may enhance the electrochemical performance. As compared to the hierarchical Cu@CuO linear heterostructure, initial Cu NWs with diameter of about 50–200 nm and length of about 40–50 μm were synthesized by the hydrazine reduction of Cu nitrate in sodium hydroxide (Supporting Information, Fig. S3 and Fig. S4). Fig. 1c displays the TEM image of the hierarchical Cu@CuO sample. It can be seen that the nanosheets are homogeneously decorated with an ordered arrangement, suggesting that this novel hierarchical structure is not simply a result of physical contact but of epitaxial growth. HRTEM image taken on the tip of a single whisker is shown in Fig. 1d. The distances between the lattice fringes is ca. 0.26 and 0.22 nm, corresponding to the d-spacing of the (111) and (200) plane of the monoclinic CuO crystal [36], which is consistent with the XRD results. As described above, the hierarchical Cu@CuO linear heterostructure can be facilely synthesized by the spontaneous oxidization route.

The well-defined hierarchical Cu@CuO linear heterostructure are then used to fabricate the CuO-PANI-rGO ternary hybrid electrode. Two-step polymerization of PANI protocol is adopted for obtaining the well dispersed, tightly anchored and homogenously contacted CuO-PANI-rGO ternary hybrid composite with high electrochemical performances. The schematic illustration for the fabrication procedure of CuO-PANI-rGO ternary hybrid electrode is shown in Scheme 1. PANI is first adsorbed on GO surface by the π - π interaction between the aromatic carbons and the phenyl groups by in situ polymerization reaction [37]. Once the as-prepared Cu@CuO linear heterostructures are added into the solution, they can be immobilized on the PANI-GO composite

surface by the benzenoid aniline groups. Subsequently, the linear architectures are wrapped by in-situ PANI coating in the second polymerization for preventing the architectures dropping out from the substrate during the electrochemistry measurements. The ternary composites are then self-assembled into a hierarchical hydrogel by the hydrothermal treatment. PANI in the ternary hybrid hydrogel serves as the charge transport channels, and high specific capacitance donor to the whole electrode matrix [38, 39]. The ternary hybrid hydrogel with unique structure and suitable components is highly expected as superior electrochemical electrode.

The composition and structure of the ternary hybrid sample was characterized by X-ray photoelectron spectroscopy (XPS), XRD, Raman, Fourier transform infrared spectroscopy (FTIR) and Thermogravimetric (TG) analysis. As shown in Fig. 2a, the XPS survey spectra indicate the presence of Cu, O, and N, as well as C from the ternary hybrid sample and the absence of other impurities. The Cu 2p XPS spectra (Fig. 2b) show two major peaks with binding energies at 932.9 and 953.2 eV, corresponding to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively, with a spin-energy separation of 20.3 eV. Meanwhile, the satellite peaks on the high binding energy side are also visible. Further, Cu2p Auger spectrum is observed at 917.6 eV as shown in Fig. S5a (see Supporting Information). The results indicate that Cu (II) oxidation state is the only species, not other copper states in the ternary hybrid sample [36, 40]. It means that the linear Cu core might be oxidized in the high temperature condition during the hydrothermal process. By using a Gaussian fitting method, the N1s spectra (Supporting Information, Fig. S5b) is fitted into four spin-orbit peaks, which are corresponding to quinoid imine (398.9 eV), benzenoid amine (399.5 eV), and protonated amine (400.5 and 401.6 eV), confirming strong $\pi-\pi$ stacking between PANI backbone and rGO nanosheets, respectively [37, 41]. The high-resolution O1s spectra shown in Fig. S5c (see Supporting Information) shows four oxygen core levels at 529.8, 530.9, 531.8 and 533.0 eV, corresponding to the oxygen species in CuO phase, rGO and the -OH species absorbed onto the surface of the nanostructures [24]. In addition, the C 1s spectra (Supporting Information, Fig. S5d) reveals the presence of three components of the carbon bond, i.e., C=C (284.8 eV), C=O (286.2 eV), and O=C-OH (288.5 eV), which are all in good agreement with the reported values [42]. XRD pattern of the products was shown in Fig. 2c. Compared to pure rGO sample, the broad peak at 20.8° is attributing to the diffraction of (110) plane of PANI crystalline phase, suggesting the successful synthesis of PANI in the composite [29]. It is worth noting that the characteristic peaks of Cu crystal are not detected in the ternary hybrid sample, indicating that the Cu template is completely oxidized during the hydrothermal reaction. In order to discover the relationship between Cu oxidation and GO reduction, the parallel experiments without PANI, or GO, and even without GO and PANI were carried out under the same hydrothermal process. The diffraction peaks of the initial Cu template are not can be seen in the prepared samples as shown in Fig. S6 in

the Supporting Information. The results indicate that the oxidation reaction of Cu core is not directly related to the reduction of GO. The reaction from Cu to CuO can be spontaneously driven by the dissolved oxygen in a high temperature. It is in agreement with the result of Fig. 2b. FTIR spectra (Supporting Information, Fig. S6a) confirm the presence of PANI in the ternary hybrid sample. The absorptions at ca. 1500.0 and 1455.0 cm^{-1} can be attributed to C–C and C–N stretching vibrations from PANI [43, 44]. Raman spectra exhibited in Fig. S6b (see Supporting Information) further confirms that the aniline monomers are successfully polymerized on rGO surface. The new sharp peak at 640 cm^{-1} is assigned to the Cu–O vibration of the monoclinic CuO crystal [45]. The peaks ring, C–N⁺ stretching in bipolaron form and C–H bending of the quinoid ring, and the appearance of the C=C stretching vibrational mode of the quinoid ring at 1582 cm^{-1} [46]. TG analysis were carried out for CuO-PANI-rGO ternary hybrid samples with various CuO contents as shown in Fig. 2d. The contents (in weight ratio) of CuO architecture in the ternary hybrid samples are about 8.0 %, 12.0 %, 16.0 % and 20.0 %, respectively.

Photographs of different self-assembled hydrogels are shown in Fig. S8a (see Supporting Information). As can be seen, the ternary hybrid sample displays the maximum column volume (2.0 cm $\times$ 3.5 cm) with minimum density (Supporting Information, Fig. S9). The uniform cross-section photograph exhibited in Fig. S8b (see Supporting Information) indicates the homogenous dispersion of the components. Morphology of CuO-PANI-rGO ternary hybrid sample was characterized by SEM image. The typical CuO-PANI-rGO ternary hybrid sample presents a porous framework structure as shown in Fig. 3a. High magnification SEM image (Fig. 3b) reveals that CuO linear hierarchical architecture is homogeneously incorporated into the interlayer galleries of graphene sheets. The EDX (Supporting Information, Fig. S10) and elemental mapping (Fig. 3c–g) analysis of typical CuO-PANI-rGO ternary hybrid sample further indicates the presence of carbon (59.2 wt%), oxygen (16.3 wt%), nitrogen (12.2 wt%) and copper (12.3 wt%). Moreover, the carbon, oxygen, nitrogen and copper elements are homogeneously distributed in the selected area.

To evaluate the electrochemical performances of the self- assembled CuO-PANI-rGO ternary hybrid samples, cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were performed using a two-electrode system in 1.0 M Na₂SO₄ aqueous solution fabricated like a sandwich as shown in Fig. 4a. For comparison, pure rGO hydrogel, PANI-rGO binary hydrogel were also studied. CV curve of the typical CuO-PANI-rGO ternary hybrid sample measured at a scan rate of 5.0 mV s⁻¹ exhibits much higher current compared to pure rGO, PANI-rGO samples, revealing the typical CuO-PANI-rGO ternary hybrid sample possesses the superior electrochemical behavior (Fig. 4b). This can be

attributed to the homogenously interfacial contact and disperse, conductive porous microstructure of the ternary hybrid electrode, which promotes the charge fast transportation and reduces the electrolyte diffusion resistance. A pair of peaks appeared on the CV curve of the typical CuO-PANI-rGO ternary hybrid sample might be aroused by the Faradaic reaction of CuO with quasi-reversible redox transition from Cu (II) to Cu (I) (0.4-0.6 V) and vice versa (0.5-0.7 V) during the scans. The Faradaic reaction occurred on the ternary hybrid electrode can be expressed as follows [47-49]:

where LEB represent the fully reduced state of leucoemeraldine, and PNB is the fully oxidized state of pernigraniline. No visible redox peaks of PANI are observed on the CV curves, implying that the charge/discharge process of PANI is over the present potential range [50]. CV curves of the typical CuO-PANI-rGO ternary hybrid sample at different scan rates from 5.0 to 100.0 mV s⁻¹ were also performed as shown in Fig. 4c. The CV curves are close to a symmetrical rectangle-like shape, indicating excellent electrochemical performance of the ternary hybrid sample. CV curves of the typical CuO-PANI-rGO ternary hybrid sample at different potential windows shows an idea capacitance with nearly mirror-image shape at a scan rate of 10.0 mV s⁻¹ even at the potential range up to 1.2 V (Fig. 4d). The voltage window from 0 to 1.2 V is set to show the stability of the ternary hybrid electrode at high potential for the realistic application. And the redox peaks become more obvious with increasing the working voltage are aroused by the improving charge transfer rate [51], which is favorable for promoting the Faradaic reaction. Different mass loading of CuO architecture in the CuO-PANI-rGO ternary hybrid samples were also studied by CV curves ranging from 8.0 wt% to 20.0 wt% as shown in Fig. 4e. The CV curves of the ternary hybrid samples with various CuO contents display good rectangularity, suggesting excellent capacitive behavior of the ternary hybrid electrodes. And the areas of the CV curves increase with CuO contents rising in the range, indicating that CuO architecture contributes the storage capacity by the pseudo-capacitive reaction for the ternary hybrid electrode. The capacitance retentions of the ternary hybrid samples with different CuO architecture contents ranging from 8.0 wt% to 20.0 wt% are gradually declined with raising the potential scan rates (Fig. 4f). It is possibly aroused by the rapid scan rates, which are not beneficial for the diffusion and migration of the electrolytic (Na⁺) ions to the inner active surface for the charge storage [32].

In order to further evaluate the electrochemical performance of the self-assembled CuO-PANI-

rGO ternary hybrid electrode, GCD measurements at the voltage range from 0 V to 1.2 V were also performed in 1.0 M Na₂SO₄ aqueous solution using the above two-electrode configuration system. GCD curves of the different electrodes obtained at a current density of 1.0 A g⁻¹ show linear and symmetrical charge and discharge profiles (Fig. 5a), indicating excellent charge storage capacity of the electrodes. The specific capacitance can be calculated for the pure rGO hydrogel (113.6 F g⁻¹), PANI-rGO binary hydrogel (343.4 F g⁻¹) and CuO-PANI-rGO ternary hybrid hydrogel (634.4 F g⁻¹) at the current density of 1.0 A g⁻¹. The capacitance improvement of the typical CuO-PANI-rGO ternary hybrid sample is attributed to the synergistic effect of the ternary components and the unique interconnected conductive porous microstructure. In the ternary hybrid sample, rGO nanosheets are interconnected to form a porous microstructure and a conductive network. It contributes to the double-layer capacitance during discharge process because the electrochemical reduction of GO is irreversible. CuO linear architecture is mainly responsible for pseudo reactions. The PANI layer not only contributes high specific pseudocapacitance to the composites, but also improves the interaction between CuO architecture and rGO nanosheets, alleviates the interface resistance for the charges smooth transportation. Specific surface area and porous structure of the as-prepared samples are measured and analyzed as shown in Fig. S11 and Table S1 in the supporting information. To further discover the advantage of self-assembled sample, the capacitive performance of the directly mixing rGO, PANI and CuO architecture sample is also surveyed. It can be calculated from Fig. S12 (in Supporting Information) that the specific capacitance is about 252.6 F g⁻¹, which is much smaller than that of the designed sample. GCD curves of typical ternary hybrid samples at different current densities (0.5–10.0 A g⁻¹) display a series symmetrical triangle curves (Fig. 5b), indicating good reversibility of the CuO-PANI-rGO ternary hybrid electrodes during charge/discharge process. Negligible voltage drop (IR drop) can be seen from the curves, indicating a really low internal resistance and excellent capacitive property of ternary hybrid electrode [52]. With further enlarging the current density from 25.0 to 100.0 A g⁻¹, a visible IR drop appeared in Fig. 5c. It suggests that the Na⁺ ions are difficult to diffuse and migrate to the active surface of the electrode at high current density. Different CuO architecture contents in the CuO-PANI-rGO ternary hybrid samples were also studied by GCD curves (Fig. 5d, Fig. S13 in the Supporting Information). The specific capacitances achieved by incorporating different CuO architecture contents at a current density of 1.0 A g⁻¹ is 408.6 (8.0 wt%), 472.3 (12.0 wt%), 548.2 (16.0 wt%), 634.4 (20.0 wt%), 598.6 (24.0 wt%) and 501.7 (28.0 wt%) F g⁻¹, respectively. At low CuO architecture mass loading (≤ 20.0 wt%), the increase of specific capacitance for the ternary electrodes is mainly ascribed to high pseudocapacitance of CuO architecture. Further increasing CuO architecture (from 20.0 wt% to 28.0 wt%), the conducting properties of the ternary electrodes would gradually decrease, resulting

to the specific capacitance declined. For the typical CuO-PANI-rGO hybrid sample with 20 wt% CuO architecture, the capacitance remained 80.9% (from 634.4 to 513.2 F g⁻¹) with increasing the current density from 0.5 to 20.0 A g⁻¹ as shown in Fig. 5e. The detailed capacitance comparison of the above three hybrid electrodes is presented in Fig. 5f. It can be seen that the typical CuO-PANI-rGO ternary hybrid sample with 20 wt% CuO content exhibits the highest capacitance. The combination of CuO, PANI and rGO into a single electrode shows excellent electrochemical performance for energy storage applications.

To discover PANI contribution to the electrochemical performance of the self-assembled CuO-PANI-rGO ternary hybrid electrode, GCD curves of the ternary hybrid samples with different PANI contents were measured. As shown in Fig. S14a (see Supporting Information), the GCD curves of the CuO-PANI-rGO ternary hybrid samples suggest that the specific capacitances gradually increased with the feeding weight ratio of aniline to GO rising. The specific capacitances achieved by incorporating different PANI contents is 328.6 (0:100), 403.4 (1:100), 494.2 (2:100) and 634.4 (4:100) F g⁻¹, respectively. Detailed comparison of the specific capacitances with PANI contents for the ternary hybrid samples was displayed in Fig. S14b (see Supporting Information). The specific capacitance obtained from the ternary hybrid sample with the feeding weight ratio of aniline to GO of 4:100 is much higher than others. The results suggest that PANI also contribute high specific capacitance for the ternary hybrid sample.

The electrochemical performance of the self-assembled CuO-PANI-rGO ternary hybrid electrode was further investigated by EIS analysis in the frequency range of 100 kHz to 0.01 Hz as shown in Fig. S15 (see Supporting Information). The Nyquist plot of the typical CuO-PANI-rGO ternary hybrid sample (Supporting Information, Fig. S15a) displays a nearly vertical line compared to others, indicating an ideal capacitive behavior. Moreover, the resistance of the ternary hybrid sample is very close to the intercept of the Nyquist curve on the real axis, suggesting a low internal resistivity and an excellent electrolyte penetration within the electrode [53]. The detailed equivalent series resistance values of different electrodes and the normalized data are achieved by using the ZsimpWin program from the Nyquist plots and listed as shown in Table S2 (see Supporting Information). It might be caused by the excellent interconnected conductivity porous microstructure of CuO-PANI-rGO ternary hybrid sample, which is favorable for promoting the electron transportation and electrolyte penetration [54]. The Nyquist plot of CuO-PANI-rGO ternary hybrid sample by incorporation of 20 wt% CuO architecture (Supporting Information, Fig. S11b) shows a maximum straight line slope at low frequency and a minimum semicircle at high frequency as compared to other samples, revealing the smallest electrode resistance and the highest charge transfer rate. As compared to other hybrids, the typical CuO-

PANI-rGO ternary composite with 20 wt% CuO content displays largest BET specific surface area ($135.6 \text{ m}^2 \text{ g}^{-1}$) with widest pore size distribution (30.0 to 200.0 nm) according to nitrogen adsorption-desorption (NAD) measurements as shown in Fig. S11 and Table S1 in the supporting information. Although the conductivity of CuO is poorer than that of PANI and rGO, the unique microstructure of the typical ternary hybrid hydrogel provides more sufficient porosity for the electrolyte rapid penetration and shorter path length for charge smoothly transfer, leading to smallest electrode resistance and the highest charge transfer rate. The Nyquist plots of CuO-PANI-rGO ternary hybrid samples with different PANI contents (Supporting Information, Fig. S15c) show the electrochemical performance gradually increased with PANI content rising.

To further evaluate the electrochemical performance of self-assembled CuO-PANI-rGO ternary hybrid electrode, energy density, power density and volumetric capacity were achieved through GCD measurements in the potential range from 0 to 1.2 V at current density of 1.0 A g^{-1} . As shown in Fig. 6, the self-assembled typical ternary hybrid device exhibits a maximum energy density of 126.8 Wh kg^{-1} with a power density of 114.2 kW kg^{-1} , and a volumetric capacity of 4.7 F cm^{-3} . The small volumetric capacity of CuO/PANI/rGO hierarchical electrode is arised from the low density. However, the result is much higher than that pure rGO electrode, CuO-rGO binary hybrid electrode, PANI-rGO binary hybrid electrode, and CuO-PANI-rGO ternary hybrid electrode with different CuO contents (Supporting Information, Fig. S16, and Table S3). The exceptional energy density is seldom available in the symmetric capacitors according to the reported values [17, 19, 20, 23, 55-59], and very close to the conventional batteries ($\sim 200.0 \text{ Wh kg}^{-1}$) [2, 4]. The excellent electrochemical performance of such CuO-PANI-rGO ternary hybrid electrode device can be ascribed to the following reasons: (1) The prominent specific capacitance as high as 634.4 F g^{-1} , which is beneficial for achieving high energy density. (2) The enlarged cell voltage range arrived to 1.2 V during the charge/discharge process. It needs to point out that the operated cell voltage of previous studies is usually no more than 1.0 V. (3) PANI combined other two components shows a unique conductivity porous microstructure, which provides high specific surface area, excellent electrical conductivity, shorter ion diffusion length and charge diffusion resistance. In order to verify the excellent electrochemical property of the ternary hybrid electrode, two of which were connected in series as shown in Fig. 7a. After charging for only 10 s at a current density of 25.0 A g^{-1} , the pattern fabricated by 33 red light-emitting diode (LED) lamps connected in parallel can be lighten for about 15 min (Fig. 7b-d, and Supporting Information, Move S1), indicating practical application of the CuO-PANI-rGO ternary hybrid electrode as high performance energy storage device.

The cycle stability is also most important characteristics for energy storage devices. The long-

term cycle stability of the typical CuO-PANI-rGO ternary hybrid sample with 20 wt% CuO architecture at a scan rate of 500.0 mV s^{-1} was shown in Fig. S17a (see Supporting Information). It can be seen that the capacitance still can remain 97.4% of its initial value after 10000 cycles, revealing its excellent cycle stability. The cycling performance of the typical ternary hybrid sample with the progressively increased potential scan rates was recorded as shown in Fig. S17b (see Supporting Information). Apparently, the typical ternary hybrid electrode exhibits stable cycling performance at each scan rates. After 9000 times of continuous cycling at varying scan rates, the potential scan rate is returned to 50.0 mV s^{-1} . Under this condition, ca. 96.0 % of the initial capacitance at 50.0 mV s^{-1} can still be recovered and maintained for another 1000 cycles without noticeable variation. The good cycle stability of the typical ternary hybrid electrode was further confirmed by comparison of the CV (Fig. S17c, Supporting Information) and GCD (Fig. S17d, Supporting Information) curves before and after 10000 cycles. Almost overlapped curves are further verified the excellent electrochemical stability of the ternary hybrid electrode due to its unique structural stability in facilitating charge transport and energy storage. The great cycle life and good rate capability of the CuO-PANI-rGO ternary hybrid electrode are important merits for the practical energy storage devices.

4. Conclusion

In summary, a novel CuO-PANI-rGO ternary hybrid electrode has been fabricated by a self-assembled method. PANI layer endows the ternary components homogenous contact, and improves the conductivity and specific capacitance for the hybrid electrode. The typical CuO-PANI-rGO ternary hybrid electrode exhibits a high specific capacitance of 634.4 F g^{-1} in $1 \text{ M Na}_2\text{SO}_4$ aqueous solution at a current density of 1.0 A g^{-1} . Moreover, it shows a prominent energy density of 126.8 Wh kg^{-1} with a power density of 114.2 kW kg^{-1} . Besides, the ternary hybrid electrode exhibits excellent electrochemical stability. The unique CuO-PANI-rGO ternary hybrid electrode with conductivity porous microstructure is expected to be a promising candidate for high performance energy storage device.

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Appendix A. Supporting information

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

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Figure Captions

Fig. 1. (a) Low and (b) high magnification SEM images, (c) TEM and (d) HRTEM graphs of the hierarchical Cu@CuO sample.

Scheme 1. Schematic illustration for the self-assembly procedure of the CuO-PANI-rGO ternary hybrid sample.

Fig. 2. (a) XPS survey spectra of the typical pure rGO sample, PANI-rGO binary hybrid sample, CuO-PANI-rGO ternary hybrid sample, (b) high-resolution XPS spectra for Cu 2p of CuO-PANI-rGO ternary hybrid sample, (c) XRD pattern of the pure rGO sample, PANI-rGO binary hybrid sample, CuO-PANI-rGO ternary hybrid sample, and (d) TG curves of the CuO-PANI-rGO ternary hybrid samples with various CuO contents.

Fig. 3. (a) Photographs of the pure rGO hydrogel, PANI-rGO binary hybrid hydrogel, and CuO-PANI-rGO ternary hybrid hydrogel, (b) cross-section photograph of the CuO-PANI-rGO ternary hybrid hydrogel, (c, d) SEM images, and (e-i) EDX mapping of total, C, Cu, O and N element of the typical CuO-PANI-rGO ternary hybrid sample.

Fig. 4. (a) Schematic of the sandwich-like electrode fabricated by CuO-PANI-rGO ternary hybrid sample in 1.0 M aqueous Na₂SO₄ electrolyte, (b) CV curves of the typical CuO-PANI-rGO ternary hybrid sample compared with rGO, and PANI-rGO samples at a scan rate of 100.0 mV s⁻¹, (c) CV curves of the typical CuO-PANI-rGO ternary hybrid sample at different scan rates from 5 to 100 mV s⁻¹, (d) CV curves of the typical CuO-PANI-rGO ternary hybrid sample at different potential windows (0–1.4 V) at a scan rate of 100.0 mV s⁻¹, (e) CV curves of the typical CuO-PANI-rGO ternary hybrid samples with different CuO mass loadings from 8.0 wt% to 20.0 wt% at a scan rate of 100.0 mV s⁻¹, and (f) Comparison of the specific capacitance retentions between the ternary hybrid samples with various CuO contents (8.0–20.0 wt%) and scan rates.

Fig. 5. (a) GCD curves of the typical CuO-PANI-rGO ternary hybrid sample compared with rGO, and PANI-rGO samples at a current density of 1.0 A g⁻¹ under the voltage range from -0.2 V to 1.2V in 1 M Na₂SO₄ aqueous solution, (b, c) GCD curves of the typical CuO-PANI-rGO ternary hybrid sample at different current densities from 0.5 to 100.0 A g⁻¹, (d) GCD curves of the typical CuO-PANI-rGO ternary hybrid samples with different CuO mass loadings from 8.0 wt% to 20.0 wt% at a current density of 1.0 A g⁻¹, (e) Comparison of the specific capacitances between the ternary hybrid samples with various CuO contents (8.0–20.0 wt%) and current densities, and (f) Comparison of the specific capacitances between the typical ternary hybrid sample with pure rGO sample, and PANI-rGO binary hybrid sample.

Fig. 6. Energy and power density plots of the typical CuO-PANI-rGO ternary hybrid electrode compared with the reported values.

Fig. 7. (a) The integral circuit device connected by two of the CuO-PANI-rGO ternary hybrid electrodes in series, (b-d) The pattern fabricated by 33 red LED lamps in parallel lighted for 0, 7.5, 5 and 15 min by the circuit device.

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