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C@KCu_7S_4 Microstructure for Solid-state Supercapacitors

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Abstract

Here we report a high-performance all-solid-state C@KCu_7S_4 hybrid supercapacitors based on the carbon (C) particles coated on the KCu_7S_4 electrode. The C@KCu_7S_4 hybrid supercapacitor (2 mg C) show good electrochemical behaviors with a large specific capacitance of 352 F g^{-1} at a scan rate of 10 mV s^{-1}, the highest energy density of 26.2 Wh kg^{-1} and the highest power density of 994.8 W kg^{-1}, still hold 86% of the capacitance after 2000 cycles. Moreover, a light-emitting diode (LED) can be lighted by three supercapacitors in series for about 3.5 min, indicating the good application prospect of using C@KCu_7S_4 hybrid supercapacitors as energy storage.

Introduction

Electrochemical capacitors (ECs), also called supercapacitors or ultracapacitors, has attracted much attention in the automotive and consumer electronics industry due

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to their high capacitance, pulse power capability, and long cycle life.[1–4] Recently, nanomaterials with high specific surface area have been widely utilized to improve the charge accumulation and ion transport in ECs.[5] Carboneous materials, such as carbon nanotubes (CNTs) and graphene, can accelerate charging-discharging of electric double-layer capacitors (EDLCs),[6-9] and have been widely used in the supercapacitors. Because of the different charge storage mechanism, ECs can be often divided into three types: electric double-layer capacitors (EDLCs), pseudocapacitors, and hybrid electrochemical capacitors. The performance of ECs is mainly determined by the electrochemical activity and kinetics of the electrodes. Therefore, to improve the energy density of ECs at high rates, it is critical to enhance the kinetics of ion and electron transport in the electrodes.[10] The hybrid supercapacitors usually combine one battery-type faradaic electrode (as energy source) with the other capacitive electrode (as power source) in the same cell.[11-12] They reveal more increased capacitance and improved energy density than EDLCs, but the cycle ability of the faradaic electrode is still limited. So it still has a great challenge to develop the most promising structure or architecture that dramatically enhance the capacity while maintaining the excellent rate capability and charge-discharge cycling life.[13] For practical applications, it is necessary to find appropriate electroactive materials and integrate them into specific device configurations, therefore, the development of new material platforms to fabricate energy storage devices becomes an indispensible and challenging task.[14-15]

The KCu_7S_4 microwire is a novel and good material of the supercapacitors and KCu_7S_4 microwire shows a good electrochemical performance. In particular, the

Mn/KCu_7S_4 hybrid supercapacitor has been reported and displayed a good electrochemical performance with a large specific capacitance of 1620 F g^{-1} at a scan rate of 1 mV/s.[16] The KCu_7S_4 consists of compound crystal lattice structure, and one of which forms quasi-one-dimensional channels and the K^+ ions occupy the channels.[16] Because of its double larger channel structure, it not only enhances the ionic and electronic transport, but also shortens the ionic diffusion path. When a bias is applied across the electrodes, the K^+ ions can well exchange with Li^+ ions.[16] So the KCu_7S_4 microwires exhibit excellent electrochemical properties.

To further improve the electrochemical behavior of the KCu_7S_4 microwire supercapacitors, a suitable material can be used to hybrid with the KCu_7S_4. Here, we display a C@KCu_7S_4 hybrid supercapacitors fabricated by coating carbon particles on the surface of the KCu_7S_4 film. It is showed that the C@KCu_7S_4 hybrid supercapacitor with 2 mg C coating achieves the outstanding electrochemical performances with a large specific capacitance of 352 F g^{-1} at a scan rate of 10 mV s^{-1}, the highest energy density of 26.2 Wh kg^{-1} and the highest power density of 994.8 W kg^{-1}. Besides, we have connected three hybrid supercapacitors units in series to light one light-emitting diode (LED) for 3.5 min (Supporting Information Fig. S2). All the experimental results indicate the promising prospect of using C@KCu_7S_4 hybrid nanostructure as supercapacitors.

Experimental

Synthesis of the KCu_7S_4 microwires

Single-crystalline KCu_7S_4 microwires were synthesized by hydrothermal method, which was reported elsewhere.[16]

Assembly of the solid-state supercapacitor

First, the KCu_7S_4 microwires electrode was prepared as follows: the KCu_7S_4 microwires were pressed into thin films in 10 MPa with laminator, and then the KCu_7S_4 film was fixed in the copper sheet with silver paste. Second, the C@KCu_7S_4 hybrid electrode was obtained as follows: (1) 1, 2, 4 mg C powder was weighed in electronic balance (accuracy = ± 0.0001 g), respectively. And then the weighed C and 2 mL deionized water were put into 3 mL centrifuge tubes, respectively. The diameter of carbon particles in the powder is about 2~5 μm. The mixtures were dispersed uniformly with ultrasonic oscillation. (2) The mixed C was dropped on the KCu_7S_4 microwires film surface by the microsyringe. And then the C@KCu_7S_4 electrode was dried in room temperature naturally. Finally, the C@KCu_7S_4 suppercapacitor was assembled by two pieces of the C@KCu_7S_4 electrodes with a separator (Whatman 8 μm filter paper) and a solid electrolyte (polyvinyl alcohol PVA-LiCl gel) sandwiched between. PVA-LiCl gel electrolyte was simply made as follows: 6 g LiCl was mixed with 60 mL deionized water and then 6 g PVA power was added. The whole mixture was heated to 85 ^oC under vigorous stirring until the solution become clear.[17] Then the solution was keep at 85 ^oC without stirring. Before the assembling, the KCu_7S_4 microwires electrodes, C@KCu_7S_4 hybrid electrodes were immersed into the PVA-LiCl solution for 5 min. After the PVA-LiCl gel solidified, the solid-state supercapacitors were prepared.

Characterization

The method of characterization was reported elsewhere.[16] In brief, the morphologies, chemical composition, and the structure of the products were characterized by field-emission scanning electron microscopy (Nova 400 Nano SEM) and XRD (BDX3200 China). X-ray photoelectron spectrometer (XPS) analysis was performed on an ESCA Lab MKII using Mg Ka as the exciting source. The electrochemical properties of the electrodes were investigated with CHI 760D electrochemical workstation.

Results and discussion

Fig. 1 shows the XRD patterns of the prepared KCu_7S_4 microwire and C@KCu_7S_4 hybrid structure. From the pattern of A, we know that all the diffraction peaks match the KCu_7S_4 structure (JCPDS: 47-1334), with the lattice constant of a=10.167Å, b=10.167Å, c=3.825Å. With regard to another weaker peak not being presented, the reason is as follows: Crystal texture of KCu_7S_4 maybe caused by the lack of weak peak and the angle of the test is rather small (10 to 80^o). For the crystals with lower copper content, a characteristic peak splitting occurs at 2θ =~35.4^o (400 and 301) and ~39.7^o (420 and 321), which is attributed to the cell variation along the c-axis.[18] Superlattice reflection induces double c axes for the KCu_7S_4 phase.[18] All the carbon diffraction peaks match the C structure (JCPDS: 41-1487) as shown in B, with the lattice constant of a=2.47 Å, b=2.47 Å, c=6.724 Å. So we can know that the carbon particles were mixed into the KCu_7S_4 microwires films. To identify the chemical status of Cu element in the samples, XPS analysis of the KCu_7S_4 microwires

was carried out. Figure S1a exhibits the XPS survey spectrum of the KCu_7S_4 microwires and the peaks of K 2p, Cu 2p, Cu 3p, Cu 3s, S 2p, S 2s, C 1s and O 1s can be clearly observed. The weak peaks of C and O may come from CO_2, H_2O and O_2 adsorbed on the surface of the sample.[19] The high-resolution XPS spectrum of Cu 2p (Figure S1b) shows the binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks at 932.3 and 952.2 eV, respectively, which are in agreement with the reported values of the main Cu^+ peak (Cu^+ binding energy =932.2 eV, 952.4 eV),[20-21] revealing Cu^{1+} ions were dominant in KCu_7S_4 microwires. Fig. 2a shows SEM images of prepared KCu_7S_4 microwires with the diameter of around 2 μm and the length up to 110 μm. Local energy dispersive X-ray spectroscopy (EDS) analysis was also conducted for the KCu_7S_4 microwires (Fig. 2b). Besides the Si signal coming from the substrate, K, Cu and S were detected from the microwires, which indicate that the main compositions of the product were K, Cu and S. The SEM images of the surface of C@KCu_7S_4 hybrid electrode are presented in Fig. 2c, from which we can know that the C particles were nearly evenly coated on the surface of the KCu_7S_4 microwires film and the sizes of them are about 2-5 μm. Fig. 2d shows the SEM image of the cross section of C@KCu_7S_4 hybrid electrode. The KCu_7S_4 microwires film has been formed porous structure which can significantly absorb electrolyte, acting as electrolyte reservoirs to facilitate ions transport between KCu_7S_4 microwires and electrolyte.

Fig. 3a shows CV curves of KCu_7S_4 microwires electrodes at various scan rates with potential window ranging from -0.8 ~ 0.8 V, and the maximum specific capacitance of 155 F g^{-1} is achieved at a scan rate of 10 mVs^{-1}. And the galvanostatic

charging/discharging curves for the KCu_7S_4 microwires electrodes at different currents are shown in Fig. S1(a), revealing that the KCu_7S_4 microwires can be used for the supercapacitors.

To improve the capacitance of the KCu_7S_4 microwires supercapacitors, we coated C particles on the surface of the KCu_7S_4 film. The C@KCu_7S_4 hybrid supercapacitors with 2 and 4 mg C coating display better electrochemical performances as shown in Fig. 3b and c, where CV curves at various scan rates respectively. The CV curves of the C@KCu_7S_4 hybrid supercapacitors with 1 mg C coating at various scan rates are presented in Fig. S2(b) (Supporting Information). From these CV curves, we can clearly see the capacitance of the KCu_7S_4 electrode is significantly improved by coating C particles. The specific capacitance of the C@KCu_7S_4 hybrid supercapacitors by coating of 1, 2 and 4 mg C particles are about 294, 352 and 191 F g^{-1} at a scan rate of 10 mV s^{-1}, respectively, and the results are shown in Fig. 3d, which are calculated by the mass of C and KCu_7S_4 microwires. The highest specific capacitance is obtained from the C@KCu_7S_4 hybrid supercapacitors with 2 mg C, which is higher than that of bare KCu_7S_4 microwires (155 F g^{-1} at a scan rate of 10 mV s^{-1}). The specific capacitance of the C@KCu_7S_4 hybrid supercapacitors with 4 mg C is lower than that with 2 mg C. Because the increase of C content may induce a larger in the film thickness, while only a thin layer of the C@KCu_7S_4 might efficiently be charged and discharged. Such improved performances of the C@KCu_7S_4 hybrid supercapacitors are mainly attributed to the C particles. Because of its large specific surface and good electrical conductivity of the C@KCu_7S_4 hybrid

electrodes, it not only expands the penetration area of the electrolyte, but also shortens the ion diffusion path. In addition, it also enhances the ionic and electronic transport through the electrode system. Fig. 4(a) shows the galvanostatic charging/discharging curves for 2mg C@KCu_7S_4 hybrid supercapacitors at different currents, which show its good linear voltage-time profiles. The energy and power densities (E and P) are calculated using equation $E = \frac{C_s V^2}{2m}$ and $P = \frac{E}{t}$, where $\boldsymbol{C_s}$, $\boldsymbol{V}$, $\boldsymbol{M}$ and $\boldsymbol{t}$ are the total capacitance, cell voltage, mass of the electrode, discharging time.[17] The Ragone plots of the C@KCu_7S_4 hybrid supercapacitor with 2 mg C is shown in Fig. 4(b), which exhibit the highest energy and power densities are 26.2 Wh kg^{-1} at a power density of 261.4W kg^{-1} and 994.8 W kg^{-1} at an energy density of 9.5 Wh kg^{-1}.

To demonstrate actual application, we connected three supercapacitors in series to light a LED (the Power is about 36 ~ 48 mW) as shown in Fig. 4 (C1-C2), indicating that the LED can be lighted for about 3.5 min. (The more details see the supporting information in Fig. S3). Fig. 4 (C3) shows the area of the electrode is about 1.2 cm^2. The long-term cycling stability of the C@KCu_7S_4 hybrid supercapacitors (2 mg C) is also examined by a cyclic charge-discharge process at a fixed current of 5 mA in Fig. 4d. The specific capacitance of the C@KCu_7S_4 hybrid supercapacitors kept almost 86 % after 2000, which reveals it has a good long-term cyclic performance. All these revealing that the C@KCu_7S_4 hybrid supercapacitor has a good electrochemical performance.

Conclusion

In summary, the C@KCu_7S_4 hybrid supercapacitor (based on coating 2 mg C on

the KCu_7S_4 electrode) shows outstanding electrochemical performances with the largest specific capacitance of 352 F g^{-1} at the scan rate of 10 mV s^{-1}, the highest energy density of 26.2 Wh kg^{-1} and the highest power density of 994.8 W kg^{-1}. In addition, it retains 86% of its initial capacitance after 2000 times cycles. Furthermore, it also can be used to light a LED for 3.5 min by three hybrid supercapacitors units in series. All these results suggest that the C@KCu_7S_4 hybrid structure has a promising potential for the high-performance supercapacitors.

Acknowledgements

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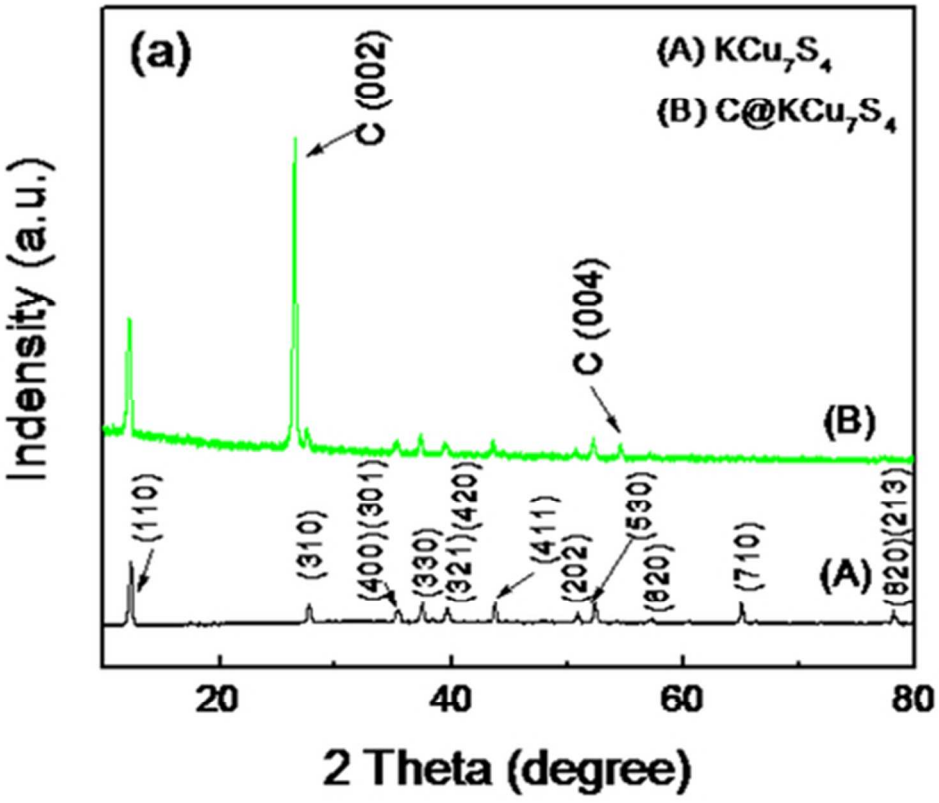
Figure Captions

Fig. 1 (a) XRD patterns of KCu_7S_4 microwires, and $C@KCu_7S_4$ hybrid electrode.

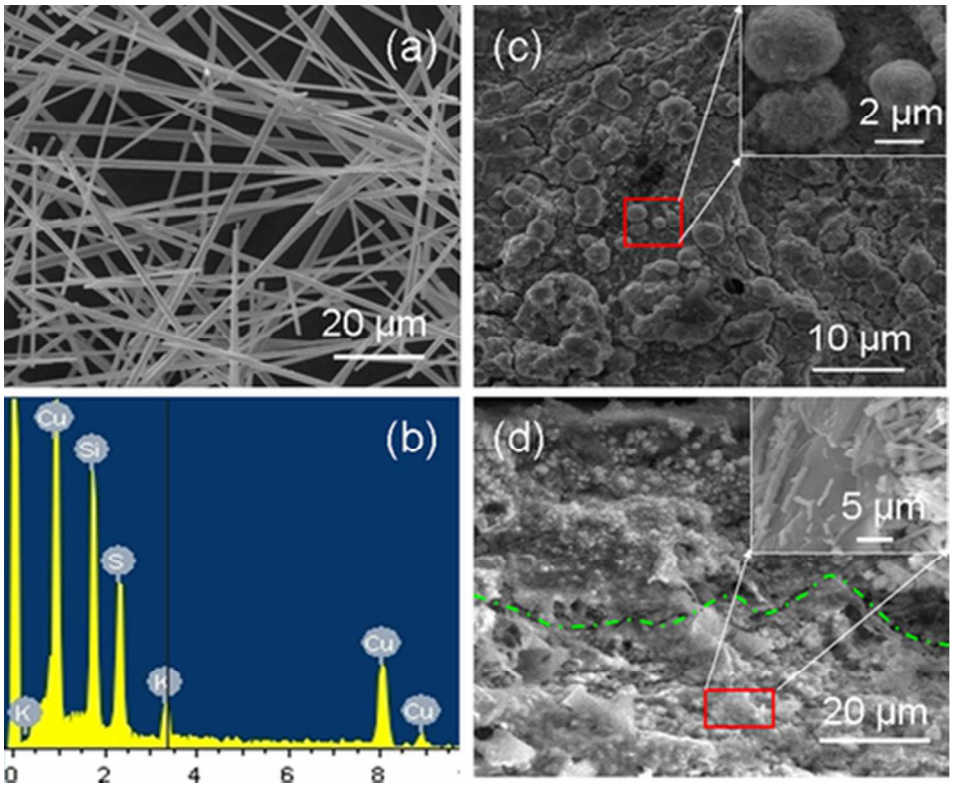
Fig. 2 (a) SEM images of KCu_7S_4 microwires. (b) EDS pattern of KCu_7S_4 microwires. (c) SEM images of the surface of $C@KCu_7S_4$ hybrid electrode. (d) SEM images of the cross section of $C@KCu_7S_4$ hybrid electrode.

Fig. 3 (a) CV curves for KCu_7S_4 microwires electrodes at various scan rates. (b), (c) CV curves for $C@KCu_7S_4$ hybrid supercapacitors at different scan rates with different C particles coating quality of 2 and 4 mg. (d) Specific capacitances of KCu_7S_4 and $C@KCu_7S_4$ hybrid electrodes at different scan rates.

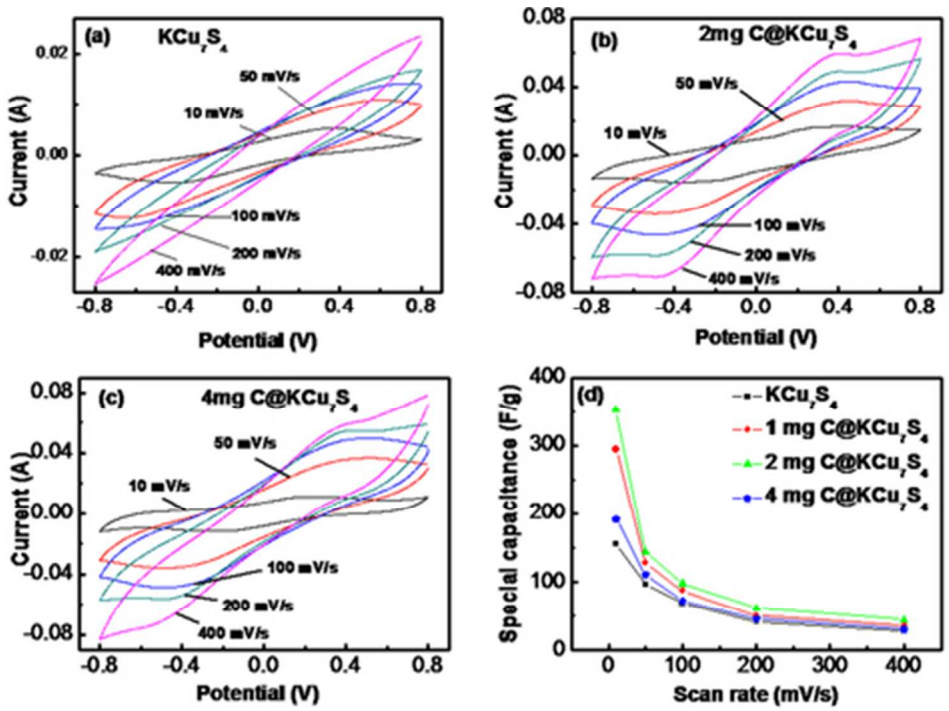
Fig. 4 (a) Galvanostatic charging/discharging curves for $C@Cu_7KS_4$ hybrid electrode at different current (the effective area of each electrode is about 1.2 cm^2). (b) Ragone plot for 2mg $C@KCu_7S_4$ hybrid supercapacitors. (C) Photograph of the light-emitting-diode (LED) driven by a device composed of three supercapacitors connected in series, (C1) in the dark and (C2) in the bright. (C3) Photograph of the capacitance region. (d) Cycle performance of $C@KCu_7S_4$ hybrid electrode over 2000 cycles at a fixed current of 5 mA.



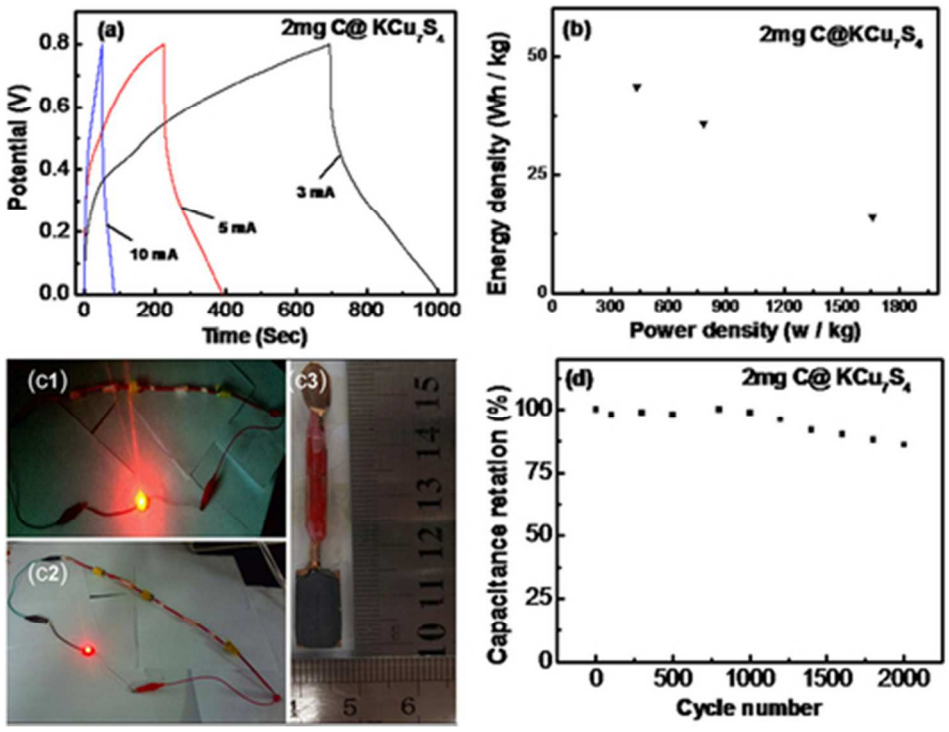
(a) XRD patterns of KCu7S4 microwires, and C@KCu7S4 hybrid electrode.
39x33mm (300 x 300 DPI)



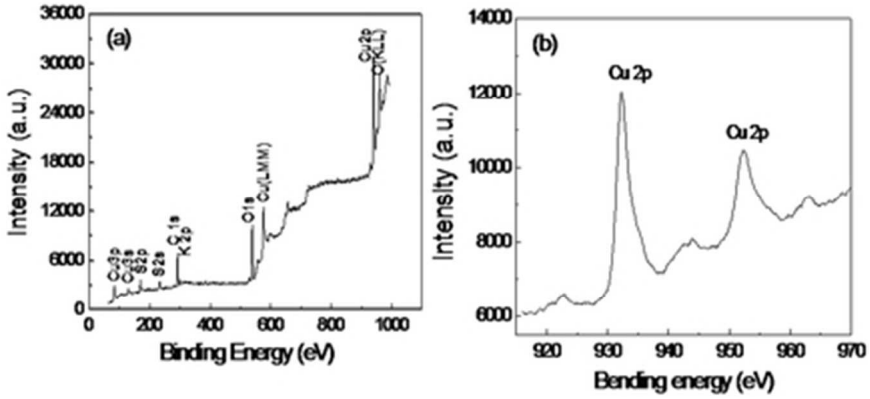
(a) SEM images of KCu7S4 microwires. (b) EDS pattern of KCu7S4 microwires. (c) SEM images of the surface of C@KCu7S4 hybrid electrode. (d) SEM images of the cross section of C@KCu7S4 hybrid electrode. 39x32mm (300 x 300 DPI)



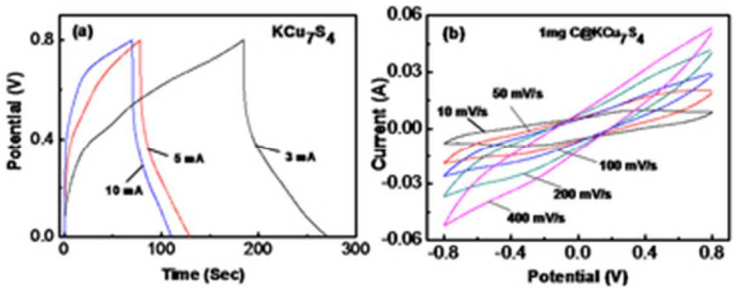
(a) CV curves for KCu7S4 microwires electrodes at various scan rates. (b), (c) CV curves for C@KCu7S4 hybrid supercapacitors at different scan rates with different C particles coating quality of 2 and 4 mg. (d) Specific capacitances of KCu7S4 and C@KCu7S4 hybrid electrodes at different scan rates.
39x29mm (300 x 300 DPI)



(a) Galvanostatic charging/discharging curves for C@Cu7KS4 hybrid electrode at different current (the effective area of each electrode is about 1.2 cm2). (b) Ragone plot for 2mg C@KCu7S4 hybrid supercapacitors. (C) Photograph of the light-emitting-diode (LED) driven by a device composed of three supercapacitors connected in series, (C1) in the dark and (C2) in the bright. (C3) Photograph of the capacitance region. (d) Cycle performance of C@KCu7S4 hybrid electrode over 2000 cycles at a fixed current of 5 mA.
39x30mm (300 x 300 DPI)



(a)XPS spectrum of the KCu7S4 microwires level. (b) XPS spectrum of Cu 2p for KCu7S4 microwires level.
36x16mm (300 x 300 DPI)



(a) Galvanostatic charging-discharging curves for KCu7S4 microwires supercapacitor at the different current (the effective area of each electrode is about 1.2 cm2). (b) CV curves of C@KCu7S4 hybrid supercapacitors at various scan rates.
30x12mm (300 x 300 DPI)

MS Title：C@KCu_7S_4 Microstructure for Solid-state Supercapacitors

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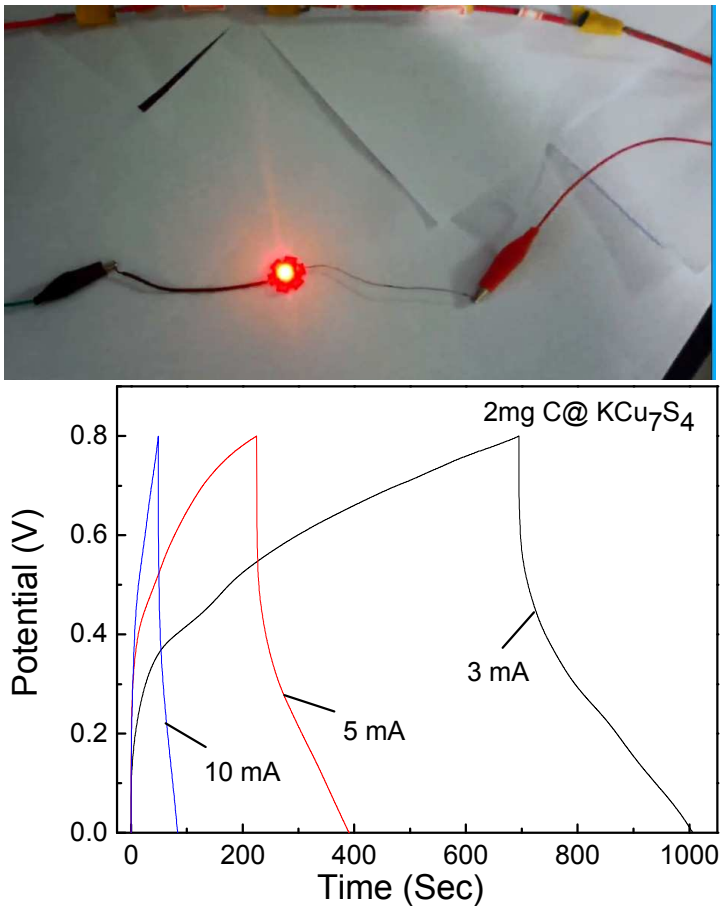
Graphical Abstract



Three C/KCu_7S_4 hybrid supercapacitors units in series can light one light-emitting diode for 3.5 min, the hybrid supercapacitors can deliver the largest specific capacitance of 352 F g^{-1} at the scan rate of 10 mVs^{-1}, the maximum power density of 994.8 kW k g^{-1}, the highest energy density of 26.2 Wh kg^{-1} and cycling stability (86% capacity retention after 2000 cycles).