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Facile synthesis of hierarchical CuS/CuSCN nanocomposite with advanced energy storage properties

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Abstract

We introduce CuS/CuSCN nanocomposites as active materials in pseudocapacitors, in which the redox reactions of both CuS and CuSCN simultaneously contribute to energy storage. This nanocomposite is prepared using in situ methodology via facile, low-energy-consuming green nanochemistry. The CuS/CuSCN nanocomposites offer high capacitance compared to their individual constituents. CuS nanorods (~ 15 nm) are anchored on the surface of CuSCN nanosheets (~ 100 nm) and they interconnect the CuSCN nanosheets, producing mesoporous nanoclusters with a large surface area, thus improving the charge transfer efficiency. The CuS/CuSCN nanocomposites possess high electrical conductivity and strong redox reactivity, and in particular, the pseudocapacitor with the compositional ratio 1:1 exhibits the highest charge transfer efficiency. Consequently, the 1:1 CuS/CuSCN active material exhibits high energy density (approximately 63 Wh/kg) and high power density (1.9 kW/kg at 9.0 Wh/kg) as a single electrode. The highest specific capacitance is measured to be 1787.3 F/g in the single electrode. Furthermore, an aqueous asymmetric hybrid supercapacitor based on the CuS/CuSCN 1:1 // activated carbon (AC) shows an approximately four times increase in power density (7.9 kW/kg), compared to the single electrode.

Keywords: supercapacitor; CuS/CuSCN; dual semiconductor active material; intercalated pseudocapacitor

1. Introduction

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In order to overcome the ever-worsening energy crisis and global warming issues owing to the over-use of fossil fuels, various potential solutions, including the development of clean and high-performance energy technologies, have been intensively studied [1, 2]. Such efforts include the development of clean energy sources such as solar cells and energy storage devices such as batteries and supercapacitors [1, 3, 4]. A new version of energy storage devices, supercapacitors, inherit the properties of both capacitors and batteries and possess significant advantages such as high specific charge density, long cyclic stability, high specific capacitance, and excellent charge/discharge behaviour [5, 6]. Two types of energy storage mechanisms are involved: electrical double-layer capacitance and redox electrochemical capacitance (or pseudo-capacitance); they enable the storage of energy in the form of electrostatic charges and reversible redox potential, respectively, at the interfaces between electrode and electrolyte.

Recently, nanostructured transition-metal sulphides such as V_2O_5/Ni_3S_2 , $Ni_3S_2@CdS$, SnS_2 , CuS/Ni_3S_2 with reduced graphene oxide (RGO), CuS-CNT (CNT: carbon nanotube), Co_2CuS_4 , and $Ni(OH)_2$ have attracted increasing attention as new electrode materials for pseudocapacitors, owing to their high electrical conductivity and stronger redox property compared to transition metal oxides [1, 5, 7-10]. CuS is one of the most promising candidates, and it is characterised by its low cost, environmentally-friendly nature, metal-like electronic conductivity (10^{-3} S cm⁻¹), and high theoretical capacity [11]. Popular synthesising methodologies of CuS are the hydrothermal method and refluxing [5, 12], which usually consume high energy during the synthesis process.

The attention of researchers has been directed to composite materials rather than a single metal sulphide compound [12]. CuS can be easily combined with carbon derivatives (CNT,

RGO, activated carbon), which, however, exhibit shortcomings such as low capacitance and low conductivity [5]. Goa et al. demonstrated that the agglomeration of graphene limits its capacitance [1]. Lu et al. reported that CuS-CNT composites with organic molecular crosslinks used as active materials unavoidably reduce the charge transfer capability [5]. Thus, there is a strong demand for a better composite material with improved conductivity and high capacitance.

In this study, we fabricate a supercapacitor using hybrid nanocomposites of CuS and copper thiocyanate (CuSCN) as a novel active electrode material. CuSCN is a remarkable inorganic p-type semiconductor [13-15], and has good charge mobility and high chemical stability [15-17]. However, combining two compounds of the same transition metal is not a usual approach to prepare composite materials, and nanocomposites of CuS/CuSCN for supercapacitor applications have not been reported to date. Recently, we reported that the conductivity of CuS/CuSCN composite is better than that of either pure CuS or CuSCN [18]. Here, the CuS/CuSCN nanocomposites are synthesised via an in situ ratio-tuneable synthesis methodology, in which the compositional ratio of the two compounds is arbitrarily controllable. The CuS/CuSCN nanostructure provides ultra-high specific capacitance by increasing the surface area of the active material exposed to the electrolyte and increasing the conductivity. We clarify the importance of the boosted charge conductivity for significantly enhancing the specific capacitance. The morphology, thermal stability, and energy storage behaviour of the developed nanocomposites are characterised.

2. Experimental

2.1. Preparation of CuS/CuSCN composite

All the chemicals were of analytical grade and used without further purification. While the conventional methods such as hydrothermal and refluxing methods use toxic hydrazine [5, 12], we used the non-toxic $Na_2S_2O_3$ as a reducing agent to prepare the CuS/CuSCN nanocomposite as presented in Fig. 1. Initially, 100 mL of 0.1 M aqueous CuSO₄ solution was mixed with 100 mL of 0.1 M aqueous Na₂S₂O₃ solution, followed by stirring for 30 min; subsequently, the colour of the solution started to change from blue to light green. Subsequently, varying amounts of 0.1 M NH₄SCN were slowly added in a drop-wise manner for several hours, and the solution turned slightly whitish owing to the growth of CuSCN crystals. Thereafter, the mixture was stirred for 24 h at room temperature, and subsequently, dark green CuS crystals grew on the CuSCN crystals. In this step, the amount of added 0.1 M NH₄SCN determined the composition ratio of CuSCN. When NH₄SCN was not added, pure CuS crystals of green colour were obtained. By adding 25 mL, 50 mL, and 75 mL of NH₄SCN in this step, the composition ratios of CuS:CuSCN were controlled to be 3:1, 1:1, and 1:3, respectively. When 100 mL of NH₄SCN was added, we could obtain pure CuSCN crystals. Thus, the compositional ratio could be easily tuned by adjusting the amount of NH₄SCN in this step. Subsequently, the dispersion was filtered and washed with deionised water and subsequently anhydrous ethanol several times each to remove the unreactants. The CuS/CuSCN powder was dried in a vacuum oven at 60 °C for 6 h.



Figure 1: Schematic diagram of the synthesising process of CuS, CuSCN, and CuS/CuSCN nanocomposites

2.2. Characterizations

The crystalline structures of the materials were determined using powder X-ray diffraction (XRD) analysis with an automated X-ray diffractometer system (D8 Focus; Bruker, Germany) with Cu-K α radiation ($\lambda = 1.5418$ Å) from 15° to 65°. The morphologies of the nanostructures of the CuS nanorods, CuSCN nanosheets, and CuS/CuSCN heterostructure were analysed using field-emission scanning electron microscopy (FE-SEM, JEM-7500F; JEOL Company, Japan) and the atomic composition was mapped using energy-dispersive X-ray spectroscopy (EDX).

The compositions of the powder materials were analysed using X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) techniques from 30 °C to 1000 °C by supplying N_2 (100 mL/min) to ascertain the stoichiometry and chemical state of the species. The XPS data were further processed using Casa-XPS software (Casa Software Ltd, UK) to determine the chemical compositions.

2.3. Electrochemical evolution measurements

The working electrode was fabricated by mixing the CuS/CuSCN composite and polytetrafluoroethylene binder in the mass ratio of 90:10. Subsequently, the mixture was dispersed in ethanol and loaded into nickel foam (MTI, Korea) as a current collector using the drop and drying method. The prepared electrode was dried at 160 °C for 2 h. A platinum electrode and Ag/AgCl electrode were used as the auxiliary and reference electrodes, respectively, and 3 M KOH solution was used as the electrolyte. The redox capacitive performances of the electrodes made of CuS/CuSCN composites were investigated using a threeelectrode system. Electrochemical impedance spectroscopic (EIS) measurements were obtained using an electrochemical workstation—VSP (Bio Logic SAS, France)—and cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) measurements were collected using another electrochemical workstation-WizECM premium-1600 (WizMAC, Korea). CV and GCD analyses were performed in the potential window of 0-0.7 V with varying scan rates, and EIS was performed under the application of 10 mV of AC voltage in the frequency range of 0.01 Hz to 100 kHz. The specific capacitance, C_s (F/g), was calculated according to the following equation:

$$C_s = \frac{I\Delta t}{m\Delta V},\tag{1}$$

where I (A) represents the discharge current, and m(g), $\Delta V(V)$, and $\Delta t(s)$ indicate the mass of the active material, potential drop during discharge, and total discharge time, respectively. Other important parameters of the performance of a supercapacitor are the specific energy density and power density, which were calculated as follows:

$$ED \ (W \cdot h / Kg) = \frac{0.5 \times C_s \times V^2}{3.6} , \qquad (2)$$

$$PD (W/Kg) = \frac{ED \times 3600}{t},$$

where V (V) is the voltage change during the discharge process after IR drop and t(s) is the discharge time.

2.4 Asymmetric supercapacitor

The CuS-CuSCN 1:1 // activated carbon (AC) asymmetric supercapacitor was fabricated to analyse the capacitive behaviour of the asymmetric full cell configuration. The CuS-CuSCN 1:1 composite coated Ni foam, 3 M KOH, grade 1 Whatman cellulose filter paper, and AC coated Ni foam were used as positive electrode, electrolyte, separator, and negative electrode, respectively. The negative electrode was prepared following the method in the literature [19]. The specific capacitance of the device was obtained from following formula:[20]

$$C_{device} = \frac{I \times \Delta t}{m_{total} \times \Delta V} \tag{4}$$

Here, C_{device} (F/g) is specific capacitance of the asymmetric supercapacitor device; I (A) and Δt (s) are the current and the time of the discharge process; m_{total} (g) is the total mass of both positive and negative electrode active materials; ΔV is the operating potential of the asymmetric device.

The energy density and power density of the asymmetric supercapacitor device were calculated using the equations: [21, 22]

$$ED = \frac{1}{2}C_{device}\Delta V^2 \tag{5}$$

$$PD = \frac{3600 \times ED}{t} \tag{6}$$

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3. Results and discussion

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3.1. Material characterizations

As shown in Fig. 1, the synthesis process is simple and non-toxic; moreover, the composition ratio of CuS and CuSCN in the nanocomposites is arbitrarily determined by adjusting the amount of NH₄SCN. The chemical reactions governing the syntheses of CuS and CuSCN were precisely described in the literature [23, 24]. For CuS synthesis, Cu^{2+} ions from CuSO₄ react with HS⁻ ions from Na₂S₂O₃ and water. In the same reaction, by adding the same molar fraction of NH₄SCN as that of CuSO₄ in a drop-wise manner, CuSCN is produced instead of CuS because SCN⁻ has a stronger affinity towards Cu¹⁺ ions. Notably, while the synthesis of CuS requires approximately 24 h, the synthesis of CuSCN occurs within a short time after adding NH₄SCN. The reason for adding NH₄SCN in a drop-wise manner is to prevent the quick growth of CuSCN grains and to obtain nanosheets of CuSCN crystals. By controlling the speed of dropping and stirring, the crystal size can be controlled to some degree. When the molar fraction of added NH₄SCN is less than that of CuSO₄, initially CuSCN nanocrystals are synthesised, and subsequently, after fully consuming NH₄SCN, CuS is synthesised. Notably, CuS nanorods are likely to grow on the surface of CuSCN nanosheets, producing hierarchical nanostructures.

Figure 2 reveals the structures of CuS, CuSCN, and the nanocomposite of CuS/CuSCN. All the samples were synthesised under the same conditions except for the concentration of NH₄SCN. On the one hand, CuS crystals have a petal-like shape (Fig. 2a), and their surface morphology is rough owing to the protruding nanorods but the core is a large lump with no pores, as indicated in the bottom image of Fig. 2a. On the other hand, fully grown micrometre-sized CuSCN crystals are prism-shaped as shown in Fig. 2b, but the small crystals are round and flat. In the case of the nanocomposite of CuS/CuSCN (Fig. 2c), larger flat CuSCN particles are

covered by smaller CuS nanorods. Owing to the lower concentration of NH₄SCN, the size of the CuSCN crystals is mostly smaller than that of the crystals in the neat CuSCN sample. Notably, the CuS nanorods do not form a petal-shaped lump crystal, but have a distinguished rod shape. The CuS nanorods cover the CuSCN particles, and many pores exist. Thus, the nanoporous structure of CuS/CuSCN composite can allow the electrolyte to penetrate into the core particles of the composite. The EDX spectrum in Supplementary Fig. S1 confirms that the material compositions are well-matched to the target chemical structures. The atomic ratios of CuS and CuSCN in the EDX analysis are also approximately matched to the chemical structures.



Figure 2: SEM images of (a) CuS, (b) CuSCN, and (c) nanocomposite of CuS/CuSCN. The bottom images are the expanded ones.

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Figure 3: (a) XRD patterns of CuS, CuSCN, and CuS/CuSCN nanocomposite, (b) TGA curves of (I) CuS nanorods; nanocomposites of ratios (II) 3:1, (III) 1:1, (IV) 1:3; (V) pure β -CuSCN nanosheets in N₂ environment. (c-f) High-resolution XPS spectra for nanocomposites with ratios (c) 3:1, (d) 1:1, (e), 1:3 and (f) β -CuSCN nanosheets for the N1s region

The combination of these dual capacitive components in nano-range is well illustrated by the crystallite sizes from the XRD patterns shown in Fig. 3a. The sharp peaks of CuS, CuSCN, and CuS/CuSCN in the XRD pattern clearly demonstrate their good crystallinity. The crystalline peaks values of CuS and CuSCN at 2θ are consistent with the peaks from the corresponding

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crystal planes shown in JCPDS cards (card no. 06–0464 for CuS and 29-0581 for CuSCN). The sharp XRD peaks of the CuS/CuSCN 1:1 nanocomposite shown in Fig. 2 indicate that the composite is also perfectly crystalline. The diffraction peaks of CuS/CuSCN are almost the same as the combination of peaks from CuS and CuSCN, indicating no change in the phase structure.

TGA analyses of the composites were performed to study the thermal behaviour and composition of their nanostructures. All the composites and CuS except CuSCN indicate that the first weight loss starts in the temperature range of 200–320 \Box , caused by the dehydration of water content. CuS nanorods decompose to Cu₂S and sulphur at approximately $400-450 \square$ (Fig. 3b-I).[25] As shown in Fig. 3b-V, CuSCN undergoes decomposition of approximately 20 % at $433-450 \Box$, producing CuCN and sulphur. The second decomposition with approximately 16 % of mass loss appears in the range of 580–720 \Box , which corresponds to the generation of CS₂ gas. [26] The TGA curves for the three nanocomposites (CuS:CuSCN = 3:1, 1:1, and 1:3 in Figs. 3b II-I, respectively) show multiple decomposition drops with varying mass loss depending on the chemical structures. The mass loss ratios corresponding to the generation of CS_2 gas increase as the composition ratio of CuSCN increases, which is consistent with the expected results. At approximately 350-500 \Box , the nanocomposites (Figs.3b II–IV) show two types of phase decompositions of the two compounds. We believe that the first drop occurs owing to the decomposition of CuSCN to CuCN and S and the second drop corresponds to the decomposition of CuS to Cu₂S and S.[25, 26] As the composition of CuSCN increases, the first drop also increases; this indicates that the compositional ratios of CuS and CuSCN in the nanocomposites are well controlled as expected.

We also performed a comprehensive XPS study to confirm the compositions of the nanocomposites. The XPS survey spectra confirm the presence of copper, sulphur, carbon, and nitrogen, and the results are shown in Supplementary Fig. S2. The accurate quantitative and qualitative analyses for CuSCN and its composites were performed with their N1s peaks using XPS, as shown in Figs. 3c-3f. The spectrum of N1s has a major peak at 398.2 eV [13], which corresponds to N in the nitrile form (N=C) with a small shoulder. The intensities of these peaks are proportional to the amount of -SCN groups, providing the information of the amount of CuSCN. The N1s peak intensities continue to increase and accurately match the concentration of CuSCN in the materials.

Recently, it was reported that the CuS/CuSCN nanocomposite has significantly improved conductivity compared to either CuS or CuSCN [18]. The creation of copper vacancies during the deposition of CuS on CuSCN particles is one of main reasons for the increase in the conductivity. Smooth interconnection between CuSCN and CuS particles in the nanocomposites also reduces the resistivity [18].

3.2. Electrochemical performance of supercapacitors

The electrochemical performances of supercapacitors with various electrodes were investigated using three-electrode systems containing 3 M KOH aqueous electrolyte. For the purpose of comparison, we also prepared a device with pure nickel metal form electrode (NF) without any active material, and another device with a manual mixture prepared by grinding both CuS and CuSCN materials in the composition ratio of 1:1. As shown in Fig. 4a, the CV curves of all the samples measured at the scan rate of 100 mV/s in 3 M KOH solution confirm that the mechanism and behaviour of charge storage are completely different from those of electrical double-layer capacitors with an approximately rectangular shape. The curves show that the

supercapacitors using CuS, CuS/CuSCN, and CuSCN electrodes are all pseudocapacitors having redox peaks. The corresponding electrochemical reactions for the CuS/CuSCN electrode redox pair can be explained as follows:

$$CuS + OH^{-} \leftrightarrow CuSOH + e^{-} \tag{7}$$

$$CuSCN + OH^{-} \leftrightarrow CuSCNOH + e^{-}$$
(8)



Figure 4: Comparison of pure CuS, CuSCN, and 1:1 nanocomposite with (a) CV curves under the scan rate of 100 mV/s with 3 M KOH electrolyte, and (b) GCD curves with the current density of 1.11 A/g. The comparison of nanocomposites with (c) CV curves under the scan rate of 100 mV/s with 3 M KOH electrolyte, and (d) GCD curves with the current density of 1.11 A/g.

As shown in the green CV curve with negligible CV integrated area in Fig. 4a, the NF itself does not contribute capacitance. Hence, the CV curves of the other electrodes are attributed to the capacitance contribution of the added active materials. The electrode containing either pure CuS or pure CuSCN has relatively low specific capacitance, as indicated by the small integrated areas of the corresponding CV curves in Fig. 4a. Notably, the electrode with the manual mixture (not composite) exhibits higher capacitance than those of either CuS or CuSCN. Further, the integrated area in the CV curve of 1:1 nanocomposite cell exhibits dramatic enhancement compared to those using other materials. Although the manual mixture and 1:1 nanocomposite have an identical composition ratio of CuS: CuSCN, the nanocomposite electrode exhibits much higher capacitance than the manual mixture electrode. The nanocomposite has a novel nanostructure of CuS nanosheets interconnected with CuSCN with a large surface area, which enhances the charge exchanging ability with the electrolyte. CuS has its cathodic peak (A_1) and anodic peak (B₁) at approximately 0.4–0.6 V and 0.2–0.3 V, respectively (see Supplementary Fig. S3a for detailed curve structure), and CuSCN has its cathodic (A_2) and anodic peak (B_2) at 0.2–0.4 V and 0.45–0.55 V, respectively (see Supplementary Fig. S3b). The CuS/CuSCN nanocomposite electrode exhibits two cathodic (A_1, A_2) and two anodic peaks (B_1, B_2) , which approximately coincide with the peaks from pure CuS and CuSCN components. Thus, it is confirmed that both CuSCN and CuS contribute to the redox response of the nanocomposite. The GCD curves in Fig. 4b exhibit clear deviation of the discharge curve from a straight line, representing a faradic redox supercapacitor discharge. The GCD curve of the nanocomposite shows the longest discharging time at the current density of 1.11 A/g. Thus, the specific capacity of the nanocomposite is remarkably larger than that of pure CuS, CuSCN, and the manual mixture. This enhancement of the capacitance of the nanocomposite may be due to the

combination of CuS and CuSCN faradic pseudocapacitance and improved conductivity. Simultaneously, the novel porous nanostructure increases the contact area between the electrode material and electrolyte and accordingly exploits the input of the electrochemical active material to the overall specific capacitance.



Figure 5: (a-c) CV curves of 3:1, 1:1, and 3:1 nanocomposites at different scan rates, respectively, and (d-f) the GCD curves of the same materials with different current densities, respectively.

In order to optimise the compositional ratio in terms of capacitive capability, the electrochemical behaviours of the three nanocomposites with varying ratios are also evaluated, as shown in Figs. 4c and 4d. The 1:1 nanocomposite exhibits the largest integrated area compared to the other two compositional ratios of 3:1 and 1:3 (Fig. 4c). Figure 4d shows the GCD test of the nanocomposites within the potential window of 0–0.7 V, and the 1:1 nanocomposite exhibits the longest discharging time compared to the 3:1 and 1:3 composites.

The specific capacitance of the 1:1 nanocomposite is 1787.3 F/g at 1.11 A/g. Thus, the specific capacity of the 1:1 nanocomposite is larger than those of the composites with different mixing ratios. This indicates that the 1:1 nanocomposite has an optimum structure with large specific surface area and excellent electrical interconnection of CuS nanorods with CuSCN nanosheets. The IR drop was 0.16 V, as shown in Fig. 4b, and all other GCD curves in Fig. 4d and Figs. 5e-f show a similar level of IR drop.

Furthermore, the GCD curves (Fig. 4b and 4e) exhibited the intercalation pseudocapacitive behaviour with KOH electrolyte, which has kinetics similar to the typical pseudocapacitive behaviour [27]. The intercalation pseudocapacitive behaviour has the properties of both pseudocapacitors and battery, and its electrochemistry is similar to that of battery [28]. The similar intercalation behaviour with the electrolyte has been reported in the supercapacitors using $CuSbS_2$ and MnO_2 [29, 30].

Figures 5a–5c show the CV curves of the nanocomposite electrodes measured at various scan rates ranging from 50 mV/s to 500 mV/s in the range of 0–0.7 V with 3 M KOH. These curves demonstrate the high rate capability and reversibility of the CuS/CuSCN nanocomposite electrode even at high scan rates. Particularly, the CV curves of the 1:1 nanocomposite (Fig. 5b) have the largest integrated area for all the scan rates than those of the other two composites (Figs. 5a and 5c). Their electrochemical behaviour was further evaluated using GCD measurements over a wide range of current densities. As shown in Figs. 5d–5f, the potential was in the range of 0–0.7 V with the current densities ranging from 1.11 to 10.5 Ag⁻¹. The multiple flat stages in the discharge part of GCD curves (Fig. 5d-5f) of CuS/CuSCN NCs appear due to the pseudocapacitive nature, indicating the redox reactions of both CuS and CuSCN [31]. These discharge curves have two independent flat stages at approximately 0.2–0.3 V and 0.45–0.55 V,

representing the flat stages of pure CuS (Supplementary Fig. S4a) and CuSCN curves (Supplementary Fig. S4b), respectively. The specific capacitances of the optimum material, i.e. the 1:1 composite, are 1787.3 Fg⁻¹, 1267.5 Fg⁻¹, 634.07 Fg⁻¹, 318.2 Fg⁻¹, 296.82 Fg⁻¹, and 259.64 Fg⁻¹ at the current densities of 1.11 Ag⁻¹, 1.48 Ag⁻¹, 2.00 Ag⁻¹, 3.32 Ag⁻¹, 6.18 Ag⁻¹, and 10.5 Ag⁻¹, respectively, as shown in Fig. 5e.

Reversibility and cycle stability are essential factors for the supercapacitor performance. For further understanding, the 1:1 nanocomposite was evaluated using GCD cycles with different current densities. As shown in Fig. 6a, the 1:1 nanocomposite at 1.11 A/g in 3 M KOH shows perfect cycle reversibility. The stability of the 1:1 nanocomposite at the current density of 10.5 A/g was measured using GCD (Fig. 6b). The 1:1 nanocomposite shows the specific capacitance retention 93.7 % after 2000 cycles, representing the exceptional cycling stability of CuS/CuSCN nanocomposite. In the first 70 cycles, the capacitance retention was larger than 100 %, which may be attributed to the gradual activation of the electrode [32].



Figure 6: (a) GCD curve of the 1:1 nanocomposite at the current density of 1.11 A/g, and (b) the cyclic performance of nanocomposites at the current density of 10.5 A/g within the potential window of 0-0.7 V (vs. Ag/AgCl) in 3 M KOH electrolyte. (c) Ragone plot of specific power vs. specific energy of the CuS/CuSCN nanocomposites within full range of all the positive electrode.

Ragone plots (power density vs. energy density) of the nanocomposites are shown in Fig. 6c. The plot shows that the pseudocapacitors using the proposed active material are located between the conventional supercapacitor and battery applications. Researchers in this field aim to achieve higher power density and high energy density simultaneously, indicated by the arrow in Fig. 6c. The devices using our nanocomposites exhibit slightly higher energy density than the conventional supercapacitors and slightly higher power density than the conventional batteries. Notably, the energy density of the pseudocapacitor using the 1:1 nanocomposite reaches approximately 62.0 W \Box h/kg at the power density of 198.4 W/kg, which is superior to that of the other CuS/CuSCN nanocomposites (40.1 W.h/kg at the power density of 182.7 W/kg in the case of the 3:1 nanocomposite, and 43.3 Wh/kg at the power density of 182.7 W/kg in the case of the 1:3 nanocomposite). The high energy density in 1:1 nanocomposite is close to the value of usual battery, as indicated in Fig. 6c, and this may be attributed to the effect of intercalation pseudocapacitive behaviours. The 1:1 nanocomposite exhibits an outstanding power density of 1873.5 W/kg at the low energy density of 9.0 Wh/kg, indicating greater power capability. According to literature, the energy density of CuS nano-hollow spheres is 47. 4 Wh/kg at 0.3 W/kg [33] and that of CuS microspheres is 15.06 Wh/kg at 392.9 W/kg [34]. Thus, the result obtained using the 1:1 CuS/CuSCN nanocomposite is much greater than that obtained using any of these materials including CuS. In particular, our material is superior to other typical supercapacitor materials; for example, the energy density of pomelo peel activated carbon is 12.8 Wh/kg at 3854 W/kg [35], that of Ni(OH)₂ nanospheres is 35.7 Wh/kg at 490 W/kg, that of $Ni(OH)_2$ /graphene composition is 48 Wh/kg at 0.23 kW/kg, and that of RuO₂/graphene composition is 14 Wh/kg at 21 kW/kg [36].

The Nyquist plot (Fig. 7) intercepts the X-axis at $R_{\rm S}$ (solution resistance) in the highfrequency area; R_S includes the sum of electrolyte solution resistance [37], intrinsic resistance of the active material, and contact resistance of the electrode-electrolyte interface [38]. The values of R_s of the 3:1, 1:1, and 1:3 nanocomposites are 2 Ω , 3 Ω , and 3.6 Ω , respectively. R_s gradually increases with the increase in CuS content of the nanocomposite from 1:3 to 3:1, which suggests that CuS acts as the interconnection agent between the composite nanoparticles. The 3:1 nanocomposite has the lowest solution resistance among the nanocomposites. The charge transfer resistance, R_{ct}, is represented by the diameter of the semicircle in the high-frequency region [38, 39]. It is evident that the 1:1 nanocomposite has the lowest R_{ct} value (0.5 Ω) as compared to the other nanocomposites (2 Ω for 3:1 and 7.2 Ω for 1:3 composites). This indicates that the 1:1 composite possesses lower charge transfer resistance. The straight line in the lowfrequency area appears owing to the ion diffusion behaviour [37]. When the concentration of CuS is gradually increased, the steepness of the slope of the curves increases, indicating faster ion diffusion and charge adsorption into the electrode surface at a high concentration of CuS [40]. Although the 1:1 nanocomposite has higher R_s than the 3:1 nanocomposite, R_{ct} dominantly influences the electrochemical performance. Hence, the 1:1 nanocomposite with the lowest R_{et} exhibits the highest electrochemical performance and the highest capacitance [41]. These results reveal that good electrical conductivity and high ion diffusion behaviour of the 1:1 nanocomposite result in its high performance as an active material for a supercapacitor. Even with a very low internal resistance, the voltage drop can be significant when the current is high, as shown in Fig. 4b.



Figure 7: Nyquist plots for the 3:1, 1:1, and 1:3 nanocomposites from left to right

To further validate the practicability of CuS-CuSCN nanocomposites for supercapacitor application, we prepared an asymmetric hybrid supercapacitor using the CuS-CuSCN cathode and an AC anode. The CV curves of the AC (see supplementary Fig. S5) and CuS-CuSCN 1:1 NC at 500 mv/s tested in the three electrode system are shown in Fig. 8a, where the AC and 1:1 NC operated at -0.8 - 0.0 V and 0.0 - 0.7 V, respectively, revealing the capability of these two electrodes. The assembled hybrid supercapacitor can be operated in 1.5 V, as confirmed in Fig. 8b. Degradation of aqueous KOH and gas generation can occur when the applied voltage exceeds 1.5 V, and so, 1.5 V was selected to investigate the electrochemical performance of the device. Fig. 8c shows that the supercapacitor can be operated from 0.0 V - 1.0 V to 0.0 V - 1.5 V at 400 mV/s. GCD curves shown in Fig. 8d clearly exhibit the perfect charge/discharge mechanism. The specific capacitance calculated from the GCD curves at different current densities showed the highest capacitance 657.86 F/g at the current density of 1.11 A/g. In other conditions, the capacitances were 538 F/g, 298.66 F/g, 274.5 F/g, 273.9 F/g and 238 F/g for the current densities of 1.48 A/g, 2.0 A/g, 3.32 A/g, 6.18 A/g and 10.5 A/g, respectively.



Figure 8: (a) CV curves for AC and CuS-CuSCN 1:1 NC electrodes at the scan rate of 500 mV/s. (b) CV curves for the CuS-CuSCN 1:1 NC//AC hybrid supercapacitor at various scan rates. (c) CV curves in different potential windows for the hybrid supercapacitor at 400 mV/s. (d) GCD curves for the hybrid supercapacitor device at various current densities. (e) Power densities as a function of current densities for the hybrid supercapacitor and a CuS-CuSCN single electrode. (f) A photograph of two CuS-CuSCN 1:1 NC//AC hybrid supercapacitors connected to 247 LEDs.

The power density as a function of current density is presented in Fig. 8e. The maximum power density of 7.87 kW/ Kg was recorded for the hybrid device at the current density of 10.5 A/g. It clearly shows that the power density increases roughly 4 times by assembling the CuS-CuSCN 1:1 NC cathode and the AC anode, compared to the single electrode measurement. It is known that carbon based material is suitable for an anode for supercapacitor with high power density [42, 43]. In addition, the use of hybrid device increases the operating potential window,

which is essential to expand its applicability. Using two hybrid supercapacitors connected in series, a panel of 247 LEDs composed of 134 red LED (L813SRD-C, Kingbright Electronics Co. Ltd., Taiwan) and 113 green LED (L813GD) was easily lighted up, as shown in Fig. 8f. The operational voltages of green and red LEDs are around 2.2 V and 1.8 V, respectively. The 247 LEDs were arranged in a parallel connection, and so, the minimum operational voltage to light the LED panel is 2.2 V. The CuS/CuSCN 1:1 NC//AC hybrid supercapacitor device has the maximum operational voltage of 1.5 V. Therefore, we connected two hybrid supercapacitor devices in series to double the maximum operational voltage, which can easily light the LED panel.

4. Conclusion

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We synthesised a dual pseudocapacitive CuS/CuSCN nanocomposite using an in-situ methodology in which the compositional ratio between the CuS and CuSCN in the nanocomposites could be controlled in a facile manner, and mesoporous CuS-covered-CuSCN nanocrystals with large surface area could be obtained. The novel hetero-nanostructure could be characterised as CuSCN nanosheets wrapped by CuS nanorods. We used the CuS/CuSCN nanocomposites as an active material for pseudocapacitors. Both CuS and CuSCN demonstrated pseudocapacitive behaviours independently and their nanocomposites achieved high electrochemical performance. Consequently, the fabricated CuS/CuSCN 1:1 nanocomposite electrode exhibited a high specific capacitance of 1787.3 F/g at 1.11 A/g and high energy density (approximately 63 Wh/kg) at the operating voltage of 0.7 V in 3 M KOH for the half-cell test. In the asymmetric hybrid cell combined by AC electrode, the specific capacitance decreased to 657.86 F/g at 1.11 A/g, but the power density increased approximately four times. The high

energy density may be partially attributed to the effect of intercalation pseudocapacitive behaviours. The supercapacitor reported in the present study has unique characteristics that exceed those of some of the best reported supercapacitors operated in aqueous electrolytes. The superior long GCD cycles demonstrated that it can be applied in both supercapacitors and batteries. Such superior capacitive behaviour is attributed to the hierarchical novel nanostructure assembled from CuS nanorods with CuSCN nanosheets. Thus, this study paves the way for the use of CuS/CuSCN electrodes in electrochemical energy storage materials with high capacity and fast rate capability.

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Table of Contents



Facile fabrication of CuS/CuSCN nanocomposite electrode for a supercapacitor with high specific capacitance (1787.3 F/g)