One-pot facile synthesis of nanorice-like structured CuS@WS₂ as an advanced electroactive material for high-performance supercapacitors

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Abstract

Binder-free nanorice-like featured CuS@WS₂ structures have been synthesized using a simple and cost-effective chemical bath deposition approach and their application as electroactive material for high-performance supercapacitors. The surface properties of morphology, structure and composition of the as-prepared electrodes are examined using the scanning electron microscopy, transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy, respectively. The nanorice-like featured CuS@WS₂ electrode exhibits nanorice-like structures, which provides the abundant active sites for redox reactions and facilitates the electrolyte diffusion. The electrochemical performance of the supercapacitor electrodes was examined by cyclic voltammetry and galvanostatic charge–discharge studies. From the electrochemical tests, the CuS@WS₂ electrode exhibits a higher specific capacitance (C_s) of 887.15 F g⁻¹ at a current density of 3.75 A g⁻¹ with greater energy density and excellent rate capability compared to bare CuS (588.0 F g⁻¹) and WS₂ (19.40 F g⁻¹) electrodes. Overall, these results demonstrate that the as-synthesized CuS@WS₂ could be a promising material for next-generation high-performance electrochemical energy storage applications.

Keywords CuS@WS₂ · Nanorice-like · Chemical bath deposition method · Supercapacitors · Specific capacitance

1 Introduction

The huge demand of the energy consumption made fossil fuels to perish earlier which enabled to rely on the most feasible energy sources such as renewable energy sources. Numerous experiments were conducted to store this energy and eventually found the more efficient energy storage devices such as supercapacitors, batteries, etc. [1–3]. These supercapacitors have some appreciable characteristics such as fast-charging capabilities, greater power densities and longer life period. Hence, they are

also termed as electrochemical capacitors that have more industrial and technical applications [4, 5]. Depending on their charge storage phenomenon, the supercapacitors are categorized into two types such as (1) electrical double-layer supercapacitors, where the capacitance occurs because of the ion adsorption/desorption in between the carbon electrode and redox electrolyte, and (2) Faraday (redox) supercapacitors, where the higher capacitances are observed at reversible faster redox reactions.

EDLC supercapacitor electrodes are widely fabricated using the porous carbon materials. At the same time, the

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pseudocapacitor electrodes are made from transition metal oxides, hydroxides, sulfides and conducting polymers, etc. For various applications in solar cells, supercapacitors and photocatalysis [6–10]. In practical applications such as electric vehicles, there are some limitations when using the high-cost transition metal oxides (RuO_2 and V_2O_5) [11, 12]. Hence, there is a greater importance to fabricate pseudocapacitors with low-cost materials. There are some reports in recent time that suggest mixing two metal oxides increases the specific capacitance and results in greater electrical conductivity [13].

Because of their good electrochemical abilities, transition metal sulfides (TMS) were found to be the good option for electrode materials in supercapacitor applications [14]. Different TMS such as CoS_x , Ni_3S_2 and CuS can be used as electroactive materials for supercapacitor applications [15–17]. Tungsten disulfide (WS_2) is one of the typical layered transition metal dichalcogenide (TMD) has found to be the efficient SC electrode material observed from its good layered structure and excellent conductivity [18–20]. Higher capacitive values can be achieved when used as nanostructured materials than bulk materials. Further, this exhibits an enhanced surface area and minimal transfer channels for ions/electrons resulting in good capacitance [21]. Though CuS has a greater usage in supercapacitor applications, there is a huge research going on the WS_2 to identify the electrochemical capacitance properties of nanostructured WS_2 [22, 23]. Tu et al. synthesized WS_2 nanostructures and showed a specific capacitance of 398.5 F g^{-1} for sheet-like WS_2 structures [24]. Pan et al. [25] synthesized a CuS -decorated Ti_3C_2 MXene for asymmetric supercapacitors and obtained a specific capacitance of 169.5 C g^{-1} at 1 A g^{-1} . Kumar et al. [26] fabricated the CuS/Cu(OH)_2 nanocomposite material for supercapacitor applications and achieved the 845.5 F/g at 1 mA/cm^2 . Raghavendra et al. [27] synthesized the CuS electrode and obtained the specific capacity of $164.053 \text{ m Ah g}^{-1}$ at 1 A g^{-1} .

Inspired from the above works, the present work reports the method of chemical bath deposition for the synthesis of nanorice-like structured CuS@WS_2 that is used for various supercapacitor applications. Further, this CBD method is very simple to operate, low cost and can be implemented for deposition of large area. This paper includes the synthesis of nanorice-like structured CuS@WS_2 electrode was prepared by CBD on the surface of Ni foam substrate and that can be employed as supercapacitor electrode material. The electrochemical studies were analyzed through cyclic voltammetry (CV) and galvanostatic charge–discharge measurements in a 3 M KOH solution using three-electrode setup. The formation of a nanorice-like structured CuS@WS_2 gives rise to better electrical conductivity, faster electrolyte diffusion and

rapid electron pathways compared to those of bare CuS and WS_2 electrode materials. As a result, the nanorice-like structured CuS@WS_2 electrode exhibits a higher specific capacitance than the bare CuS and WS_2 electrodes.

2 Experimental

2.1 Materials

All the chemicals used in the synthesis were of analytical grade purchased from Sigma-Aldrich. Copper sulfate (CuSO_4), urea ($\text{CH}_4\text{N}_2\text{O}$), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), sodium tungstate dihydrate (Na_2WO_4) were used as obtained.

2.2 Preparation of CuS , WS_2 and CuS@WS_2 electrodes

In the synthesis of CuS , 0.1 M of CuSO_4 , 0.4 M of urea and 0.4 M of $\text{Na}_2\text{S}_2\text{O}_3$ were dissolved in 70 mL of deionized (DI) water and constantly stirred for 30 min. Nickel (Ni) foams (of size $2 \times 5 \text{ cm}^2$) cleaned by ultrasonication process were dipped in the as-prepared CuS solution and kept in the oven at 90°C for 6 h. After cooling to room temperature, the Ni foams were further washed with ethanol, DI water, dried in oven at 60°C for overnight and stored properly.

For WS_2 electrode preparation, 0.1 M of Na_2WO_4 , 0.4 M of urea and 0.4 M of $\text{Na}_2\text{S}_2\text{O}_3$ were dissolved in 70 mL of DI water. The ultrasonically cleaned Ni foams were immersed in the as-prepared WS_2 solution and kept in hot-air oven for 90°C for 6 h. Further, the obtained electrodes were washed properly and dried in the oven at 60°C for 12 h and used for electrochemical measurement.

In the synthesis of CuS@WS_2 , 0.1 M of CuSO_4 , 0.4 M of urea and 0.4 M of $\text{Na}_2\text{S}_2\text{O}_3$, 0.1 M of Na_2WO_4 were dissolved in 70 mL of DI water and further stirred for 30 min to make a constant homogenous solution. Then, Ni foams were immersed in this solution and kept in oven at 90°C for 6 h. After this, the Ni foams were washed with ethanol and DI water and dried in the oven at 90°C for 12 h and stored properly for the characterizations.

2.3 Characterization

The electrode morphology can be characterized by field emission scanning electron microscopy (FE-SEM S2400, Hitachi). Transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS, KBSI, Busan) was performed to examine the chemical states of the elements. The phase structure of the copper sulfide-based electrode was analyzed by X-ray diffraction (XRD, D/Max-2400, Rigaku) using $\text{Cu K}\alpha$ source.

2.4 Electrochemical measurements

The electrochemical measurements were carried out using BioLogic-SP150 workstation, and the experimental tests were performed using a three-electrode setup with CuS@WS₂ as the working electrode, Ag/AgCl as the reference electrode and Pt wire as the counter electrode. The aqueous 3 M KOH is used as the electrolyte. The specific capacitance (C_s , F g⁻¹), energy density (E , W h kg⁻¹) and power density (P , W kg⁻¹) of the as-prepared electrodes were calculated using the following equations:

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

$$E = \frac{0.5 \times C_s \times \Delta V^2}{3.6} \quad (2)$$

$$P = \frac{E \times 3600}{\Delta t} \quad (3)$$

where I , Δt , ΔV and m represent the current (A), discharge time (s), potential window (V) and mass (g) of the electro-active material, respectively.

3 Results and discussion

The CuS, WS₂ and CuS@WS₂ electrode materials were grown on Ni foam surface using facile chemical bath deposition method. SEM and TEM analysis were performed to study the morphologies of the electrodes under a variety of magnifications, as shown in Fig. 1. From Fig. 1a, the CuS nanoparticles were grown steadily on the surface of the Ni foam substrate. In Fig. 1a1, a2, every nanoparticle was composed of the very small tiny bundle of widespread nanorice-like particles. Further, it is observed that from

Fig. 1 Low- and high-magnification SEM images of (a, a1, a2) CuS, (b, b1, b2) WS₂ and (c, c1, c2) composite CuS@WS₂ electrodes on Ni foam surface

Fig. 1b, b1, b2 that the smooth surface of agglomerated nanosheets was covered over the Ni foam surface homogeneously exhibiting an intermediate resistance of WS₂ electrode. Concurrently, Fig. 1c, c1, c2 shows that the nanorice-like particles were distributed on the Ni foam.

The structure of as-prepared material on Ni foam was further confirmed by TEM characterization. Figure 2 depicts the TEM images of the as-prepared CuS, WS₂ and CuS@WS₂ electrodes, respectively. The TEM image of CuS material exhibits the agglomerated nanoparticle structures (Fig. 2a, a1). Figure 2b, b1 shows the TEM image of nanosheet-like structures. The TEM image in Fig. 2c, c1 represents the homogenous distribution of nanorice-like structures which were interconnected with each other. The TEM results are consistent with the SEM studies. The observed unique surface area and unique structure are advantageous to electrolyte diffusion and electron transfer, which promotes the electrochemical activity of CuS@WS₂.

XRD analysis was performed to obtain the crystal structures and phase purity of CuS, WS₂ and CuS@WS₂ precursors as shown in Fig. 3. The XRD peaks for CuS observed at 21.78°, 27.71°, 31.82°, 35.05°, 43.14° and 53.27° 2θ were given to the (0 0 4), (1 0 1), (1 0 3), (1 0 4), (1 0 6), and (1 1 4) planes of the CuS peaks (JCPDS No: 01-079-2321), respectively [28]. For WS₂, the peaks observed at 14.3°, 32.7°, 39.5°, 57.3°, 60.0°, 70.1° and 78.3° were given to the (0 0 2), (1 0 0), (1 0 3), (1 1 0), (0 0 8), (1 0 8) and (2 0 0) planes of the hexagonal-phase WS₂ structure (JCPDS 84-1398), respectively [29].

Fig. 3 XRD pattern of CuS, WS₂ and composite CuS@WS₂ electrode on Ni foam

XPS was performed to find the chemical composition and the oxidation states of the various compounds like CuS, WS₂, CuS@WS₂. Figure 4a shows the XPS survey spectrum of the CuS, WS₂, CuS@WS₂ electroactive materials on Ni foam. The bare CuS and WS₂ survey scans show the existence of Cu and S and W and S signals. More interestingly, the composite of CuS@WS₂ survey spectrum shows the presence of the Cu, W and S elements. The Ni peak in the XPS survey spectrum is

Fig. 2 TEM images of (a, a1) CuS, (b, b1) WS₂ and (c, c1) CuS@WS₂ electrodes

Fig. 4 **a** XPS survey spectra of as-prepared CuS, WS₂ and CuS@WS₂ electrodes on Ni foam. High-resolution XPS spectra of **b** Cu2p, **c** W4f and **d** S2p signals in CuS@WS₂ electrodes

due to the background of Ni foam. Figure 4b shows the high-resolution Cu2p spectrum. The Cu2p spectrum exhibits the two strong peaks at the binding energies of 934.0 and 953.87 eV, which are assigned to Cu2p_{3/2} and Cu2p_{1/2}, respectively [30]. The difference in binding energy of these two peaks was approximately 19.87 eV. These peaks can be ascribed to the Cu²⁺ state in CuS structures. Figure 4c depicts the high-resolution XPS spectrum of W signal. The W elements are typical W⁴⁺ profile at 33.3, 35.7 and 39.7 eV and are assigned to the W4f_{7/2}, W4f_{5/2} and W5p_{3/2} states [31]. The high-resolution spectrum of the S 2p, characteristic of the S²⁻ species, is observed at 161.78 and 163.03 eV and is ascribed to the S2p_{3/2} and S2p_{1/2}, respectively [32]. The XRD and XPS

studies confirm that the CuS@WS₂ nanostructures were successfully grown on the Ni foam surface.

The energy storage performance of the CuS, WS₂ and CuS@WS₂ was analyzed by CV, GCD and EIS measurements. The electrochemical properties of the CuS@WS₂ were tested using three-electrode setup in 3 M KOH electrolyte. The KOH electrolyte was found to have very high ionic conductivity; hence, it is the most widely used electrolyte for supercapacitor applications [33]. In the three-electrode setup, platinum wire was selected as the counter electrode, Ag/AgCl as the reference electrode and the Ni foam coated with CuS@WS₂, CuS and WS₂ as the working electrodes at various conditions. Figure 5a shows the comparative CV curves of CuS, WS₂ and CuS@

Fig. 5 **a** Comparison CV curves of the CuS, WS₂ and CuS@WS₂ electrodes at the scan rate of 10 mV s⁻¹. CV curves of the **b** CuS, **c** WS₂, **d** CuS@WS₂ electrodes at different scan rates of 10–50 mV s⁻¹ in 3 M KOH solution

WS₂ electrodes at a constant scan rate of 10 mV s⁻¹. Interestingly, the CuS@WS₂ electrode exhibits the higher potential window range of -0.4 to +0.7 V, which is larger than the CuS (-0.4 to +0.6 V) and WS₂ electrode (-0.4 to +0.6 V). As shown in Fig. 5a, all the electrodes exhibit a pair of redox peaks, which might be attributed to reversible Faradaic redox reactions. Obviously, CuS@WS₂ electrode achieves the larger integration than that of CuS and WS₂ electrodes, which is attributed to the synergistic effect of redox reactions associated with CuS and WS₂ materials in composite electrode, thereby achieving superior energy storage performance. Moreover, CV tests were conducted for CuS, WS₂ and CuS@WS₂ electrodes at various scan rates of 10–50 mV s⁻¹ and the corresponding CV profiles are shown in Fig. 5b–d. With the increase in scan rate, the peak current increases and also exhibits the similar CV shape with redox peaks, which indicate that the capacitance characteristics are mainly governed by Faradaic

redox reactions. Furthermore, the anodic peak in positive direction and cathodic peak in negative direction were shifted with increasing the scan rate because the charge transfer kinetics limits the reaction [34]. From the following CV curves, composite CuS@WS₂ electrode was found to be the excellent energy storage material when compared to the CuS and WS₂ electrodes.

In addition, galvanostatic charge/discharge (GCD) measurements were conducted to examine the charge storage performance of the as-prepared electrodes. Figure 6a shows the GCD plots of as-developed CuS, WS₂ and CuS@WS₂ electrodes at various current densities within the potential window of 0 and +0.4 V. Based on GCD plots and Eq. (1), the specific capacitance values of the CuS@WS₂ composite, CuS and WS₂ are illustrated in the following table.

The specific capacitance decreased gradually with increasing current density from 3.75 to 15.0 A g⁻¹ due to

Fig. 6 GCD curves of the **a** CuS, **b** WS₂ and **c** CuS@WS₂ composite electrodes at different current densities of 6.25, 7.5 and 8.75 A g⁻¹ in 3 M KOH solution. **d** Specific capacitance as a function of current density

the resistance of the electrode and insufficient Faradaic redox reaction at high current densities. The higher specific capacitance of CuS@WS₂ was attributed to its higher surface area with the improved surface morphology of nanostructures [35] (Tables 1, 2).

The energy density and power density are the two important parameters for supercapacitors in real-time applications. Based on the as-obtained specific capacitance values, the energy and power densities of the CuS, WS₂ and CuS@WS₂ electrodes were calculated and the resulting Ragone plot is shown in Fig. 7. The energy density of the composite CuS@WS₂ material was found to be 19.16 W h kg⁻¹ at a power density of 750 W h kg⁻¹, which is much higher than the CuS and WS₂ electrodes, respectively. Consequently, we concluded that the CuS@

Table 1 Specific capacitance values of the CuS, WS₂ and CuS@WS₂

Current density (A/g)	Specific capacitance (F/g)		
	CuS	WS ₂	CuS@WS ₂
3.75	588.0	19.40	887.15
5.0	536.2	19.5	683.37
6.25	424.37	16.40	743.59
7.5	350.25	14.06	650.43
8.75	279.56	12.46	590.18
10.0	216.0	12.75	536.75
11.25	158.90	9.0	488.25
12.5	132.18	7.18	426.25
13.75	60.15	6.18	382.25
15.0	30.37	5.25	337.87

Table 2 Comparison table of recently reported similar works to CuS@WS₂

Material	Capacitance	Current density	References
Ti3C2/CuS	169.5 C g ⁻¹	1 A g ⁻¹	[25]
CuS/Cu(OH) ₂	845.5 F/g	1 mA/cm ²	[26]
h-CuS	83 m ² g ⁻¹	–	[36]
CuS	597 F g ⁻¹	1 A g ⁻¹	[37]
CuS@WS ₂	887.15 F g ⁻¹	1 A g ⁻¹	This work

Fig. 7 Ragone plots of the CuS-, WS₂- and CuS@WS₂-based electrodes

WS₂ exhibited a good energy density and power density in supercapacitor applications.

4 Conclusion

In summary, the synthesis of nanorice-like structured CuS@WS₂ nanoparticles was successfully prepared in 3 M KOH electrolyte in the three-electrode system by using a facile chemical bath deposition method. In comparison with other electrodes, such as CuS and WS₂, the CuS@WS₂ electrode showed excellent electrochemical properties including specific capacitance of 887.15 F g⁻¹ at 1 A g⁻¹. The energy density of the composite CuS@WS₂ material was found to be 19.16 W h kg⁻¹ at a power density of 750 W h kg⁻¹, which is much higher than the CuS and WS₂ electrodes, respectively. Since there are a huge number of Faradaic reaction active locations in the contact area with the electrolyte, the CuS@WS₂ electrode supports faster redox reactions and hence it delivers an excellent electrochemical behavior. Therefore, from the detailed

analysis, the CuS@WS₂ electrode referred to as a battery-type electrode material can be a potential electrode for high-performance supercapacitor applications.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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