

One-step synthesis of graphitic-C₃N₄/ZnS composites for enhanced supercapacitor performance

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Abstract

A series of graphitic-C₃N₄/ZnS (g-C₃N₄/ZnS) supercapacitor electrode materials have been prepared via a one-step calcination process of zinc acetate/thiourea with different mass ratios under nitrogen atmosphere. The optimized g-C₃N₄/ZnS composite shows a highest specific capacitance of 497.7 F/g at 1 A/g and good cycling stability with capacitance retention of 80.4% at 5 A/g after 1000 cycles. Moreover, g-C₃N₄/ZnS composites display an improved supercapacitor performance in terms of specific capacitance compared to the pure g-C₃N₄ and ZnS. In addition, our designed symmetric supercapacitor device based on g-C₃N₄/ZnS composite electrodes can exhibit an energy density of 10.4 Wh/kg at a power density of 187.3 W/kg. As a result, g-C₃N₄/ZnS composites are expected to be a prospective material for supercapacitors and other energy storage applications.

Keywords: g-C₃N₄/ZnS; Supercapacitor; One-step calcination; Energy storage

1 Introduction

Supercapacitors as energy storage devices exhibit better cycling performance, faster charge-discharge rate and higher power density than existing batteries and traditional capacitors, thus attracting great attention in recent years [1-4]. Generally, there are two classes of supercapacitors based on the different charge storage mechanism: electrical double layer capacitors (EDLCs) and pseudocapacitors [2]. Carbon-based materials are employed as electrode materials for EDLCs [5]. However, the specific capacitance is usually very low [6]. Meanwhile, transition metal oxides and hydroxides used for pseudocapacitors suffer from low specific power density [7-9]. In recent years, metal sulfides have aroused more interest from researchers toward their applications as electrode materials for pseudocapacitors due to their two or more valence states and high theoretical capacity [10-12]. Among these, zinc sulfide (ZnS) has been widely used in energy storage devices because of its advantages of good electrical conductivity, electronic properties and stability [13-15]. Nonetheless, ZnS-based electrode materials still suffer from relatively low specific capacitance. A good way to solve the as-mentioned issue is to design the hybrid electrode with a combination of carbon-based materials and pseudocapacitive materials. Compared to single-phase electrode material, the composite structure can improve the supercapacitor performance [16]. The g-C₃N₄ carbon materials with excellent mechanical strength and thermal conductivity show good performance in many fields such as wastewater detoxification [17], H₂ production [18], fuel cells [19], and supercapacitors [20]. To the best of our knowledge, g-C₃N₄/ZnS composites have been widely investigated in the photocatalytic field [21-23]. However, no reports about the supercapacitor

performance studies of g-C₃N₄/ZnS composites have been recorded.

In the current work, g-C₃N₄/ZnS composites have been synthesized via a facile calcination method and their applications for supercapacitors are investigated for the first time. With an optimal composition, the as-prepared g-C₃N₄/ZnS composites show much better electrochemical performance with a specific capacitance of 497.7 F/g at 1 A/g than the pristine g-C₃N₄ and ZnS, respectively. More importantly, the symmetric g-C₃N₄/ZnS//g-C₃N₄/ZnS supercapacitor device can achieve an energy density of 10.4 Wh/kg at a power density of 187.3 W/kg.

2 Experimental

2.1 Synthesis of g-C₃N₄/ZnS composites

A specific amount of zinc acetate (0.005, 0.02, 0.05 and 0.1 g) and 1 g of thiourea were ground sufficiently and then annealed at 500 °C for 2 h in the tube furnace at a ramp rate of 10 °C/min under a nitrogen atmosphere. After being cooled down to room temperature, the yellow powder was obtained. Based on different mass ratios of zinc acetate/thiourea in the reactants, the final samples were labeled as ZTx, where *x* are 0.005, 0.02, 0.05 and 0.1, respectively. For comparison, the pure g-C₃N₄ (denoted as ZT0) was also synthesized under the same condition without the addition of zinc acetate. In addition, the nanostructured ZnS (denoted as ZS) was prepared according to the previously reported method for electrochemical performance comparison [21].

2.2 Fabrication of electrodes

The active materials (as-prepared samples), polyvinylidene fluoride (PVDF) and carbon black were mixed in a mass ratio of 75:15:10 in *N*-methylpyrrolidone (NMP) solvent to form a slurry. Afterward, the slurry was coated onto the nickel foam (2 cm × 1 cm) and then dried at 40 °C for 12 h in a vacuum oven. The mass loading of active materials is ~2.7 mg/cm².

2.3 Characterizations

The morphological studies were carried out using scanning electron microscopy (SEM, ZEISS Sigma). X-ray diffraction (XRD, Rigaku Ultima IV) with Cu-K α radiation source ($\lambda = 1.541 \text{ \AA}$) was used to identify the phase structure of the prepared composites. The chemical bonding states of the composites were analyzed by X-ray photoelectron spectroscopy (XPS, PHI QUANTUM 2000). The BET surface area measurements were done by N₂ adsorption-desorption method at 77 K using Micromeritics Tristar-3020.

2.4 Electrochemical measurements

The electrochemical performance was tested in 6 M KOH aqueous solution using both a conventional three-electrode and two-electrode configurations. For the three-electrode system, the electrode prepared above, platinum foil and Hg/HgO electrode were used as the working, counter and reference electrodes, respectively. For the two-electrode system, two identical g-C₃N₄/ZnS composite electrodes were used to assemble a symmetric supercapacitor device with polymer filtering membrane (Celgrad 3501) as the separator. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) tests were conducted on a CHI660E electrochemical station (Chenhua Corp. Shanghai). The EIS tests were performed over the frequency range from 0.01 to 100,000 Hz at the open circuit potential with an AC voltage of 5 mV. The specific capacitance (*C_s*, F/g) for single electrode was calculated according to the following equation [24]:

$$C_s = 2I \int V dt / \left(m \cdot V^2 \Big|_{V_i}^{V_f} \right) \quad (1)$$

whereas for the symmetric supercapacitor device, the cell capacitance (*C_{cell}*, F/g) was calculated based on

$$C_{\text{cell}} = 2I \int V dt / \left(M \cdot V^2 \Big|_{V_i}^{V_f} \right) \quad (2)$$

where *I* (A) is the constant current, *t* (s) is the discharge time, *V* (V) is the total potential difference with initial and final values of *V_i* and *V_f*, respectively, *m* (g) is the weight of active materials for single electrode, and *M* (g) is the weight of active materials for both two electrodes. The energy density (*E*, Wh/kg) and power density (*P*, W/kg) were estimated by:

$$E = C_{\text{cell}} \times V^2 / (2 \times 3.6) \quad (3)$$

$$P = (3600 \cdot E) / t \quad (4)$$

3 Results and discussion

Fig. 1(a-e) shows the SEM micrographs of $g\text{-C}_3\text{N}_4/\text{ZnS}$ composites. A sheet-like structure similar to graphene can be observed from sample ZT0. However, all composites containing ZnS show spherical agglomerate clusters. Meanwhile, a large number of gaps between clusters can be noted, which can achieve a high specific surface area and provide a channel for the movement of electrolyte ions. The HRTEM image of the ZT0.02 composite is shown in Fig. 1(f). In comparison to the data in JCPDS, the lattice fringes with a spacing of 0.336 nm and 0.312 nm belong to the (002) plane of $g\text{-C}_3\text{N}_4$ (JCPDS No. 87-1526) and the (111) plane of cubic ZnS (JCPDS No. 05-0566), respectively, which can be further corroborated by XRD. To further confirm the presence and dispersion state of elements in the $g\text{-C}_3\text{N}_4/\text{ZnS}$ composites, HRTEM mapping was performed, and the results are shown in Fig. 1(g-j). It is evident that C, N, S and Zn elements are visible and well-dispersed distributions.

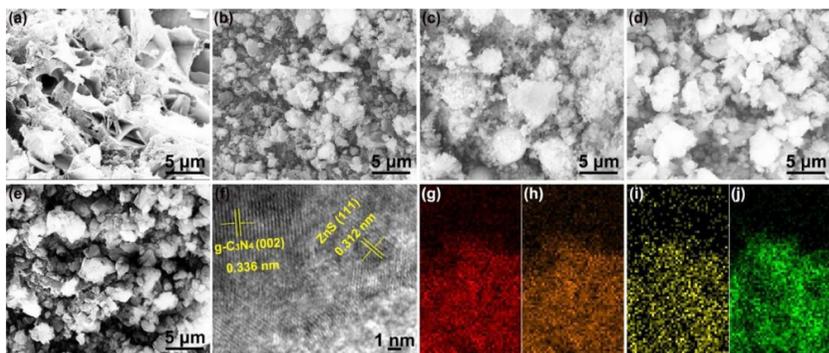


Fig. 1 SEM images of (a) ZT0, (b) ZT0.005, (c) ZT0.02, (d) ZT0.05 and (e) ZT0.1 composites. (f) HRTEM image and HRTEM mapping of (g) C element, (h) N element, (i) S element and (j) Zn element of the ZT0.02 composite.

alt-text: Fig 1

Fig. 2(a) presents the XRD patterns of all the composite samples. The strong peak at 27.5° and the weak peak at 13.1° correspond to the (002) and (100) planes of $g\text{-C}_3\text{N}_4$ (JCPDS No. 87-1526), respectively [25]. However, the characteristic diffraction peaks of ZnS cannot be observed from the composite samples ZT0 and ZT0.005. With the further increase in the mass ratio up to 0.02 and above, four additional diffraction peaks at around 28.5° , 33.1° , 47.5° , and 56.3° are found to match well to the (111), (200), (220), and (311) planes of cubic ZnS (JCPDS No. 05-0566) [14]. As shown in Fig. 2(a), a shift from $g\text{-C}_3\text{N}_4$ to $g\text{-C}_3\text{N}_4/\text{ZnS}$ is clearly seen with increasing mass ratio of zinc acetate/thiourea, demonstrating the formation of $g\text{-C}_3\text{N}_4/\text{ZnS}$ composites. The absence of any other impurity peaks exhibits no other crystalline impurity phase (ZT0.02 and ZT0.05). Nevertheless, for the ZnS rich composite ZT0.1, the impurity peaks indexed to ZnO are observed because of the oxidation of ZnS.

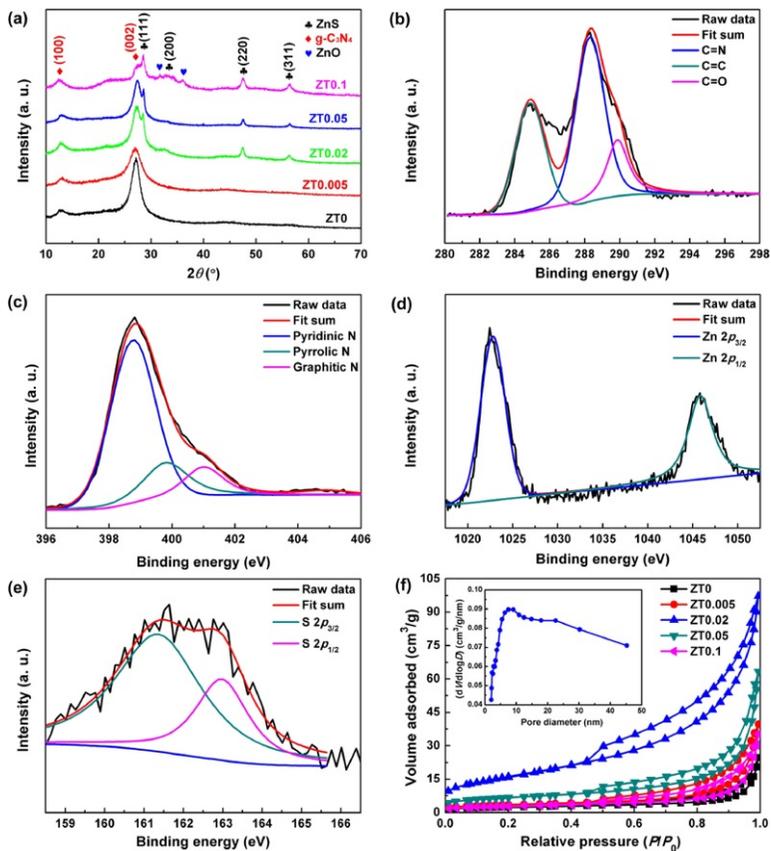


Fig. 2 (a) XRD patterns of the $g\text{-C}_3\text{N}_4/\text{ZnS}$ compositions. (b) C 1s, (c) N 1s, (d) Zn 2p and (e) S 2p XPS spectra of ZT0.02 composite. (f) The N_2 adsorption-desorption isotherms of the $g\text{-C}_3\text{N}_4/\text{ZnS}$ compositions (the inset shows the BJH pore size distribution of ZT0.02 composite).

alt-text: Fig 2

In order to investigate the chemical bonding states of $g\text{-C}_3\text{N}_4/\text{ZnS}$ composites, all the composites were characterized by XPS technique and only the XPS spectrum of a representative sample ZT0.02 is shown. As depicted in Fig. 2(b), the primary peaks at 284.6 and 289.9 eV are ascribed to the C=C and C=O components of the atmosphere, respectively. In addition, the peak at 288.6 eV can be assigned to the C–N bonds of $g\text{-C}_3\text{N}_4$ [26]. The peaks at 398.6, 400.2, and 401.3 eV in Fig. 2(c) correspond to three different types of chemical states of N 1s, manifesting the existence of C–N=C, (N–(C)₃), and C–N–H groups, respectively [27]. Fig. 2(d) shows the presence of Zn 2p_{1/2} and Zn 2p_{3/2} components that have binding energies of 1045.6 and 1022.7 eV, respectively [28]. In Fig. 2(e), the S 2p_{3/2} (161.4 eV) and S 2p_{1/2} (162.8 eV) lines indicate the existence of S²⁻ [29]. The XPS results again confirm the formation of $g\text{-C}_3\text{N}_4/\text{ZnS}$ composites, which is in good agreement with the XRD results.

Fig. 2(f) displays the N_2 adsorption-desorption isotherms of $g\text{-C}_3\text{N}_4/\text{ZnS}$ compositions. The N_2 adsorption-desorption isotherms of all composite samples are classified as type IV with an H3-type hysteresis loop in the relative pressure range from 0.45 to 1.0, which is an adsorption-desorption characteristic of mesoporous materials (2–50 nm). The BJH pore size distribution of the ZT0.02 sample (inset of Fig. 2f) further confirms the mesoporous structure. The formation of porous structure is ascribed to the aggregation of $g\text{-C}_3\text{N}_4/\text{ZnS}$ composites. The specific surface areas of all composite samples are shown in Table 1. The ZT0.02 sample possesses a higher specific surface area of 59 m²/g than other composites. It is believed that a large specific surface area is beneficial to improve the supercapacitor performance [30,31].

Table 1 Specific surface areas of the $g\text{-C}_3\text{N}_4/\text{ZnS}$ compositions.

alt-text: Table 1

Sample	ZT0	ZT0.005	ZT0.02	ZT0.05	ZT0.1
Specific surface area (m ² /g)	9	12	59	24	10

To evaluate the electrochemical performance of the composite electrodes, all the electrochemical tests were carried out in a typical three-electrode system. Fig. 3(a) illustrates the CV curves of the composite electrodes at a scan rate of 100 mV/s in a potential range from -0.1 to 0.8 V (versus Hg/HgO). The CV curve of the ZT0 sample (pure g-C₃N₄) presents a typical quasi-rectangular shape without redox peaks, which is in consistent with the literature reported [20]. However, a couple of obvious redox peaks similar to pure ZnS appear upon the addition of zinc acetate, showing a pseudocapacitive behavior. Therefore, the redox peaks can be explained by the valence state conversion between ZnS and ZnSO as proposed by Pu et al. [32]. Moreover, the integrated areas under the CV curves increase with the incorporation of more ZnS when the mass ratio of zinc acetate/thiourea is less than 0.02. However, the further increase of zinc acetate content leads to a decrease of the integral area. The same trend is also observed in specific capacitance because it is proportional to the integrated area of CV curves [33]. The GCD curves of the composite electrodes at a current density of 1 A/g are shown in Fig. 3(b). It is noted that the ZT 0.02 composite electrode shows the longest discharge time, again confirming the superior electrochemical performance. Furthermore, the voltage drop of the ZT0.02 composite electrode is about 0.12 V, implying a small internal resistance [34]. The specific capacitances are summarized and compared in Fig. 3(c). Notably, the ZT0.02 composite electrode exhibits the highest specific capacitance of 497.7 F/g at 1 A/g, which is in accordance with the CV evaluation. The enhancement in specific capacitance can be attributed to the porous structure and the higher specific surface area, which can not only promote the fast diffusion of ions from the electrolyte to the electrode, but also can provide more active sites for redox reactions. The EIS of the composite electrodes was measured and the Nyquist plots are shown in Fig. 3(d). The inset shows the corresponding equivalent circuit model. As shown in Fig. 3(d), the ZT0.02 composite electrode shows the lowest charge-transfer impedance, indicating a fast charge transfer process for the electrons and ions into the inlayer of active materials [35], which guarantees excellent rate performance. Clearly, ZT0.02 composite electrode shows better capacitive performance than others due to the nearly vertical slope at the low frequency section [36].

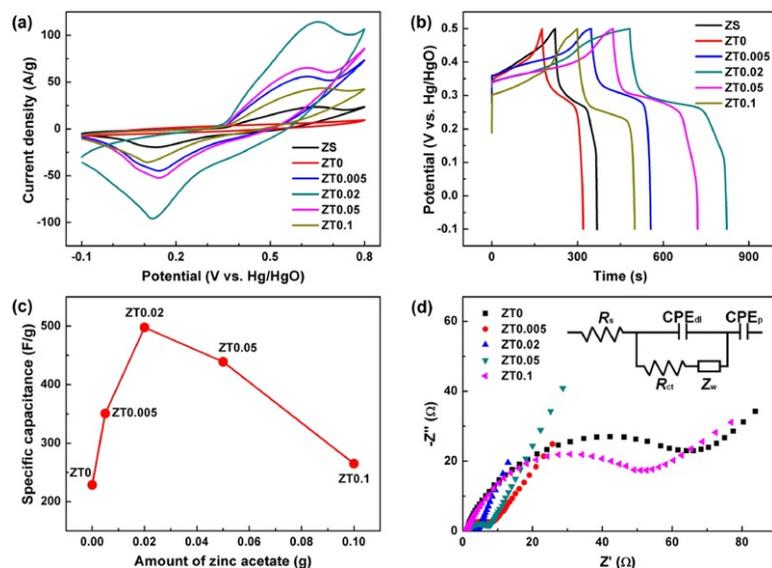


Fig. 3 (a) CV curves at a scan rate of 100 mV/s, (b) GCD curves at a current density of 1 A/g, (c) Comparison of specific capacitances at a current density of 1 A/g, and (d) EIS analysis (the inset shows the corresponding equivalent circuit model) of the composite electrodes.

alt-text: Fig 3

The ZT0.02 composite electrode is selected as a representative candidate for further electrochemical investigation. Fig. 4(a) shows the CV curves of the ZT0.02 composite electrode at various scan rates of 10–100 mV/s. The redox peaks still exist even at a scan rate of 100 mV/s, suggesting good reaction reversibility and outstanding rate performance. The GCD curves of the ZT0.02 composite electrode at different current densities are shown in Fig. 4(b). All the GCD curves show the obvious discharge plateaus, further demonstrating the pseudocapacitive behaviour [35]. The specific capacitances of the ZT0.02 composite electrode derived from the discharge curves are shown in Fig. 4(c). The specific capacitances for the ZT0.02 composite electrode are 497.7, 466.8, 401.5 and 349.7 F/g at 1, 2, 5 and 10 A/g, respectively, which is much higher than those of pure g-C₃N₄ and its composites (see Table 2), and ZnS (11.3 F/g at 0.5 A/g) [13]. Obviously, the specific capacitance of the ZT0.02 composite electrode still remains as high as 349.7 F/g even at a high current density of 10 A/g, which remains 70.2% of the initial value at 1 A/g. The decrease

in specific capacitance at high current density is attributed to the resistance of the electrode and the insufficient Faradaic redox reaction of active materials [24]. The cycling stability of the ZT0.02 composite electrode is also shown in Fig. 4(d). It can be seen that the ZT0.02 composite electrode exhibits a 20% loss of the initial specific capacitance at 5 A/g after 1000 charge-discharge cycles, indicating a good cycling stability.

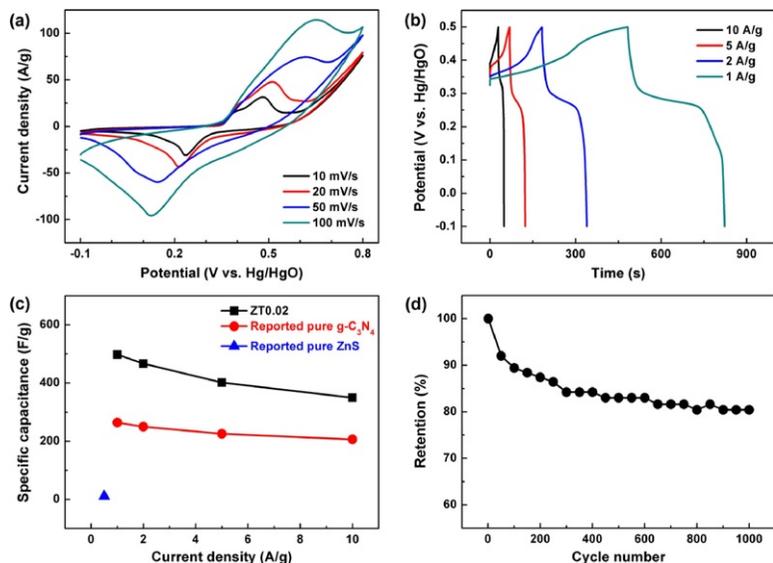


Fig. 4 (a) CV curves at different scan rates, (b) GCD curves at different current densities, (c) Comparison of specific capacitances at different current densities, and (d) cycling stability at a current density of 5 A/g of the ZT0.02 composite electrode.

alt-text: Fig 4

Table 2 Performance comparisons of the present work with other electrode materials based $g\text{-C}_3\text{N}_4$ and its composites.

alt-text: Table 2

Electrode	Specific capacitance	Cycling performance	Refs
ZnS/ $g\text{-C}_3\text{N}_4$	497.7 F/g at 1 A/g	80.4% after 1000 cycles at 5 A/g	This work
$g\text{-C}_3\text{N}_4$ nanofibers	263.8 F/g at 1 A/g	93.6% after 2000 cycles at 1 A/g	[20]
Tubular $g\text{-C}_3\text{N}_4$	233 F/g at 0.2 A/g	90% after 1000 cycles at 0.2 A/g	[37]
$\text{Ni}(\text{OH})_2/g\text{-C}_3\text{N}_4$	445.6 F/g at 1 A/g	71.5% after 1000 cycles	[38]
$\text{MnO}_2/g\text{-C}_3\text{N}_4$	211 F/g at 1 A/g	Unchanged after 1000 cycles at 2 A/g	[39]
$\alpha\text{-Fe}_2\text{O}_3/g\text{-C}_3\text{N}_4$	167 F/g at 1 A/g	Remarkable long-term cycling stability	[40]
$\text{Fe}_3\text{O}_4/g\text{-C}_3\text{N}_4$	56.7 F/g at 1 A/g		[41]

To further explore the feasibility of $g\text{-C}_3\text{N}_4/\text{ZnS}$ composite electrodes for practical application, we developed a symmetric supercapacitor device by clamping together two pieces of $g\text{-C}_3\text{N}_4/\text{ZnS}$ composite electrodes separated by a polymer filtering membrane (Celgrad 3501) in 6 M KOH aqueous electrolyte. Fig. 5(a) shows the CV curves of the symmetric supercapacitor device at different scan rates. The increase of current density with respect to the increase in scan rate can be seen. Moreover, the shapes of CV curves show no obvious changes even at higher scan rate, indicating good rate capability. The cell capacitances of the symmetric supercapacitor device at various current densities are calculated from the GCD curves (Fig. 5b). The symmetric supercapacitor device achieves a high capacitance of 92.8 F/g at a current density of 0.5 A/g and can still maintain 59.2 F/g even at a high current density of 5 A/g, holding a capacitance retention of 63.8%. The cycling performance of the symmetric supercapacitor device is evaluated by GCD test at a current density of 5 A/g, as presented in Fig. 5(c). After 1000 cycles, the cell capacitance can retain 77.8%

of the initial value. Fig. 5(d) shows the comparison of the relationship between power density and energy density of the symmetric supercapacitor device to other metal sulfides. A high energy density of 10.4 Wh/kg is obtained from the symmetric supercapacitor device at a power density of 187.3 W/kg, which is not outstanding but exceeds those of most metal sulfides, such as MoS₂ nanospheres and CuS nanoplatelets [42,43].

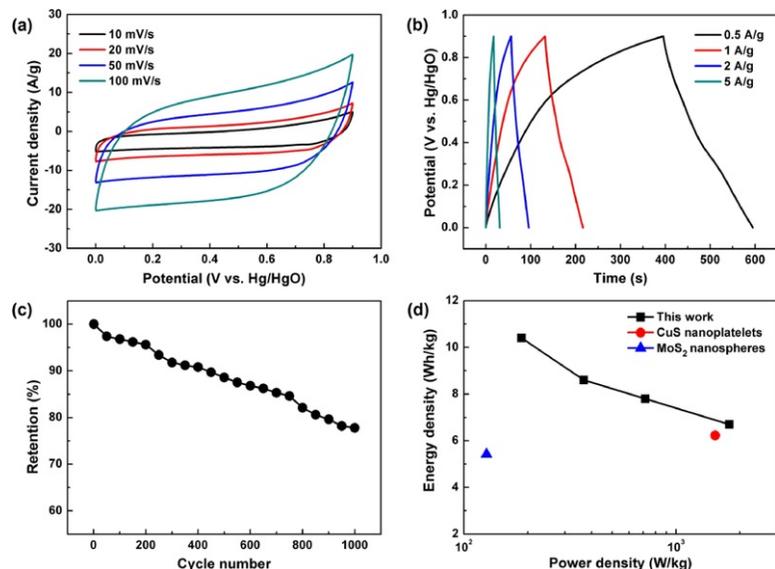


Fig. 5 (a) CV curves at different scan rates, (b) GCD curves at different current densities, (c) Cycle performance at a current density of 5 A/g, and (d) Ragone plots of symmetric g-C₃N₄/ZnS//g-C₃N₄/ZnS cell.

alt-text: Fig 5

4 Conclusions

In summary, we have synthesized a series of g-C₃N₄/ZnS composites using a feasible controlled one-step calcination method. A specific capacitance of 497.7 F/g at 1 A/g, with good rate capability (70.2% retention from 1 A/g to 10 A/g) and excellent cycling stability (80.4% retention at 5 A/g after 1000 cycles), is achieved for the final obtained g-C₃N₄/ZnS composite electrode in 6 M KOH aqueous electrolyte. In addition, g-C₃N₄/ZnS composite electrodes deliver an enhanced supercapacitor performance compared to the pristine g-C₃N₄ and ZnS. Furthermore, the symmetric supercapacitor device assembled from two pieces of g-C₃N₄/ZnS composite electrodes shows a high energy density of 10.4 Wh/kg at a power density of 187.3 W/kg. These results suggest that g-C₃N₄/ZnS composites can be used as electrode materials for supercapacitor applications.

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Highlights

- A series of g-C₃N₄/ZnS composites were prepared by one-step calcination process.
 - Supercapacitor performance of g-C₃N₄/ZnS composites is shown for the first time.
 - Maximum specific capacitance of 497.7 F/g is achieved at 1 A/g.
 - The composites show an enhanced supercapacitor performance than g-C₃N₄ and ZnS.
 - A symmetric supercapacitor device is developed and shows remarkable performance.
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Queries and Answers

Query: Please confirm that given names and surnames have been identified correctly.

Answer: Yes