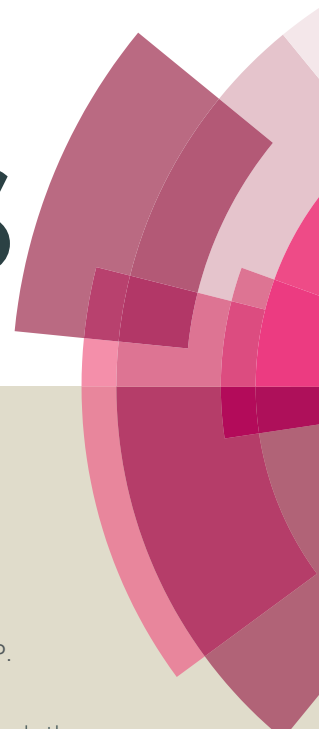


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Graphic Abstract

Synthesizing Highly Conductive Cobalt Sulfide Hydrangea Macrophylla Using Long Carbon-Chain Sulfur Source for Supercapacitors

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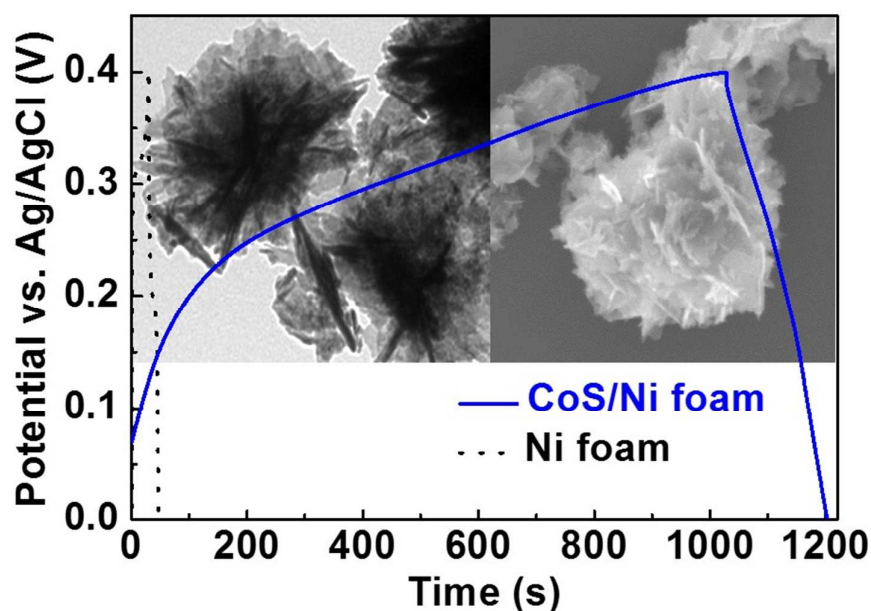
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Abstract

Cobalt sulfide has attracted much attention as the electroactive material for the supercapacitor (SC) because of its high capacitance and cost-effective features. A novel three-dimensional cobalt sulfide hydrangea macrophylla nanostructure with a thin carbon layer growing on the surface has been successfully synthesized by using a simple one-pot method with the addition of 1-dodecanethiol as the sulfur source connected with long carbon chains. The cobalt sulfide hydrangea macrophylla architecture is composed of several two-dimensional (2D) nanopetals intertwined together and thin carbon layers in the surrounding of the nanopetals. A high specific capacitance (C_F) of 324.17 F/g is obtained for the cobalt sulfide hydrangea macrophylla-based SC electrode measured by cyclic voltammetry (CV) at a scan rate of 10 mV/s, due to the large surface area for charge accumulation and faradic reactions, as well as the high conductivity for charge transportation respectively benefited from the 2D nanopetals and the carbon layers. The high C_F value achieved in this study opens a window to the morphology design for realizing highly effective pseudocapacitors.

Keywords: Cobalt sulfide; Cyclic voltammetry; Electrochemical impedance spectroscopy;

Hydrangea macrophylla; Pseudocapacitors; Supercapacitors

1. Introduction

Supercapacitor (SC) is a kind of storage device which respectively combines the feature for batteries and conventional capacitors of high power density and high energy storage capability. Nowadays, SCs have been developed for various applications owing to the advantages of high specific power density, fast dynamic charge propagation, long cycle life, and environmental friendliness.¹⁻⁴ Pseudocapacitors store charges *via* redox-based faradaic reactions at the interface of the electrode materials and the electrolyte, and therefore the higher capacitance can be delivered as compared to the electric double layer capacitors (EDLCs).⁵⁻⁷

On the other hand, due to the potential properties of cost effectiveness and the high specific capacitance (C_F), cobalt sulfides have been considered as one of the most promising pseudocapacitor electrode materials,⁸⁻¹³ but the poor conductance and mechanical instability of cobalt sulfide block its practical application.^{14, 15} Therefore, various morphologies with their promising features were synthesized to attain larger surface area and better conductivity respectively for accelerating electrons/ions accumulation and charge transportation to enhance the performance of the resulting SCs.¹⁶⁻¹⁸ Wang *et al.* synthesized three-dimensional (3D) cobalt sulfide hierarchitectures using a facile template-free solvothermal synthesis method as the electroactive material and obtained a C_F value of 555 F/g at a current density of 5 mA/cm² for the pertinent SC electrode.⁸ Luo *et al.* used a microwave-assisted heating

method to synthesize flower-like CoS nanostructures for the application of SCs and obtained a C_F value of 586 F/g at a current density of 1 A/g.⁹ Wan *et al.* used a hydrothermal method to prepare cobalt sulfide nanotubes and obtained a C_F value of 285 F/g at a current density of 0.5 A/g and good cycling stability for the resulting SC electrode.¹¹ Ji *et al.* prepared sphere-like cobalt sulfide nanocrystals with porous surfaces by a modified molten-salt synthesis method under mild reaction conditions and a C_F value of 654 F/g at a current density of 0.5 A/g was attained due to the high surface area and porosity structure.¹³ However, lots of the well-established structures of cobalt sulfide were designed to achieve high surface area to increase the C_F value,^{8, 9, 11, 14, 19-21} but the low conductivity of cobalt sulfide still limits its application. Many researchers tried to combine the carbon materials with cobalt sulfide for further improving the electrochemical capability for the resulting SCs.^{15, 22, 23} Qu *et al.* added the precursors of β -CoS_{1.097} directly in the solution containing graphene oxide to synthesize the cobalt sulfide nanoparticles decorated by graphene.¹⁵ Lin *et al.* synthesized Co₉S₈/3D graphene composite by using a glucose-assisted hydrothermal reaction with the solution containing glucose, the precursors of Co₉S₈, and the 3D graphene.²² Ramachandran *et al.* prepared the CoS/graphene nanocomposite by simply adding graphene sheets in the solution containing the CoS precursors during the synthesizing process.²³ However, the distribution of cobalt sulfide and the carbon material in the composite is relatively random by merely mixing the carbon material in the precursor solution.

In this study, a novel cobalt sulfide hydrangea macrophylla nanostructure was

synthesized *via* a simple one-pot method with the addition of 1-dodecanethiol to attain high surface area and good conductivity features. Rather than directly adding graphene or graphene oxide in the precursor solution of cobalt sulfide for simple mixing, 1-dodecanethiol was used as the carbon and sulfur source which was added during the formation of cobalt sulfide to grow a uniform carbon layer on the surface of cobalt sulfide. The similar structure has been reported before, but the application was merely on the Li storage device.²⁴ To further extend the application of this material, we tried to apply it on the SC to evaluate the electrochemical performance. The cobalt sulfide hydrangea macrophylla is composed of two-dimensional (2D) nanopetals with thin carbon layers growing on the surface of the architecture. The cyclic voltammetry (CV) and galvanostatic charge-discharge (GC/D) measurements were applied to evaluate the pseudo-capacitive properties. A C_F value of 324.17 F/g was obtained for the cobalt sulfide hydrangea macrophylla-based SC electrode at a scan rate of 10 mV/s. The electrochemical impedance spectroscopy (EIS) was also utilized to estimate the conductivity and the interfacial resistance of the cobalt sulfide and the electrolyte. To the best of our knowledge, this is the first report to synthesize the cobalt sulfide hydrangea macrophylla nanostructure with a thin carbon layer and investigate the electrochemical performance of the pertinent SCs.

2. Experimental

2.1 Materials

All the materials were used as received without any further purification. Cobalt(II) acetylacetonate ($\text{Co}(\text{acac})_2$, 99%, nitrogen flushed), 1-dodecanethiol (98%), oleylamine (C18 content 80-90%, nitrogen flushed) and hexane ($\geq 99\%$, for analysis) were purchased from Acros. Oleic acid ($\geq 99\%$, anhydrous) was obtained from Sigma. Potassium hydroxide (KOH, analytical reagent grade) was brought from Fisher.

2.2 Synthesizing cobalt sulfide hydrangea macrophylla and preparing the electrode for supercapacitors

The cobalt sulfide hydrangea macrophylla nanostructure was synthesized by using a modified method referring to the literature.²⁴ First introducing 0.2 mmol $\text{Co}(\text{acac})_2$, 1 ml oleic acid, and 5 ml oleylamine to a three-necked flask under stirring at 100 °C with an Ar flow for 30 mins. Following adding 1 ml 1-dodecanethiol in the solution and raising the temperature to 230 °C. Subsequently refluxing the solution at the same temperature and then cooling down the solution to the room temperature. Washing the dark precipitates by hexane and centrifuging them repeatedly. Drying the samples at 50 °C in a vacuum oven for 4 h and then annealing the sample under an Ar atmosphere at 350 °C for 1 h to improve the crystallinity. The chemical reactions for forming the cobalt sulfide were proposed in **Scheme 1**. The 1-dodecanethiol represented by the R-S-H group was participated in the last reaction to produce the R-S-Co-S-R group, in which R is donated as the carbon layer. The R-S-H and R-S-Co-S-R groups were circled by the red squares in reaction (III). These chemical reactions indicate the functions of the sulfide and carbon

sources of 1-dodecanethiol. For the preparation of the SC electrode, firstly dispersing the sample in the deionic water under ultrasonic vibration, and then depositing the resulting solution on the nickel foam (110PPI, thickness = 1.05 mm, Innovation Materials Co., Ltd, Taiwan) in the area of 1 cm² by utilizing a drop coating method. Finally drying the sample at 60 °C in a vacuum oven overnight to obtain the SC electrode.

2.3 Material characterization and electrochemical measurements

The field-emission scanning electron microscopy (FE-SEM, Nova NanoSEM 230, FEI, Oregon, USA) and the transmission electron microscopy (TEM, JEM-1230 and JOEL2100F, JEOL, Tokyo, Japan) were utilized to respectively observe the surface morphology and the structure of cobalt sulfides. The high-resolution transmission electron microscopy (HRTEM, JEM2100) was applied to examine the lattice of the samples. The X-ray diffraction (XRD, X'Pert³ Powder, PANalytical) was used to analyze the composition and phase of the sample. The specific surface area of the sample was estimated by using the N₂ adsorb/desorb isotherms and the Brunauer–Emmett–Teller (BET) theorem. The CV and GC/D measurements were conducted by applying a potentiostat/galvanostat (PGSTAT 204, Autolab, Eco–Chemie, the Netherlands) carried out with a three-electrode electrochemical system, where the cobalt sulfide/nickel foam was used as the working electrode, a Pt wire was used as the counter electrode, and an Ag/AgCl/saturated KCl electrode was used as the reference electrode in a 6 M KOH solution. The CV measurements were conducted in the voltage range of 0 to 0.4 V (vs. Ag/AgCl/saturated KCl) at different scan rates. The GC/D

measurements were collected in the potential range of 0 to 0.4 V (vs. Ag/AgCl/saturated KCl) at a current density of 0.5 A/g. The EIS was carried out using a potentiostat/galvanostat (PGSTAT 204, Autolab, Eco-Chemie, the Netherlands) equipped with an FRA2 module under the open-circuit potential (OCP).

3. Results and discussion

3.1 The growth of the cobalt sulfide hydrangea macrophylla

To understand the formation of cobalt sulfide hydrangea macrophylla, the growth mechanism is proposed and the schematic description was illustrated in **Scheme 2**. When the reaction begins at a relatively lower reaction temperature, the nucleation occurs at the saturated concentration of the precursors. Due to the thermodynamic preference, larger aggregations in the spherical shape would be produced in this stage. Subsequently the dissolution as well as the assembly growth of cobalt sulfide occur at a higher reaction temperature. The surface of the spherical aggregations plays as the nucleation site, and the nanocrystalline grows by consuming the ingredients of Co^{2+} and S^{2-} in the solution on these high-energy nucleation sites to produce the angular architectures. Via the precipitation solubility equilibrium in the solution due to the high intrinsic anisotropic properties, the initial formation of the layered 2D nanopetal structures starts with these angular architectures. This phenomenon can be referred as the famous Ostwald ripening process. When the reaction time keeps increasing and attains 230 °C, the initial spherical

aggregations would be used up owing to the Ostwald ripening and mass diffusion processes, and at the same time several nanopetals would be formed in the solution. The nanopetals continuously become thinner, and the further growth of the 2D nanosheets lead to the appearance of the hydrangea macrophylla nanostructure.⁸

3.2 The morphology and the crystallinity of the cobalt sulfide hydrangea macrophylla

The SEM images of the self-synthesized cobalt sulfide in the low and high magnitudes were respectively shown in **Figure 1(a)** and **1(b)**. A hydrangea macrophylla structure was observed with the size of around 300 to 500 nm in the diameter, comprising by several 2D nanosheets with the width of around 50 to 70 nm. The flat nanosheets are expected to provide high surface area for faradic reactions. On the other hand, the TEM images of the cobalt sulfide in the low and high magnitudes were shown in **Figure 1(c)** and **1(d)**, respectively. The highly ordered hydrangea macrophylla structure with several 2D nanopetals growing from the center was observed, and the carbon layers existing outside the 2D nanopetals can also be found in the light regions. To further investigate the morphology of self-synthesized cobalt sulfide, the magnified HRTEM image was examined as shown in **Figure 1(e)**. A lattice spacing of 0.262 nm was found and the carbon layers were clearly observed with the thickness of around 3 to 5 nm in this image. On the other hand, the composition and the crystallinity of the self-synthesized cobalt sulfide were investigated in the XRD patterns as shown in **Figure 1(f)**. The peaks of (220), (311), (222), (400), (331), (511), (440), (622), (731), and (800) referred from

JCPDS no. 19-366 corresponding to the cobalt sulfide patterns were observed in this figure, indicating the pure composition of the cobalt sulfide. It is inferred that the crystallinity of the carbon layer is poor since the peaks for carbon cannot be detected from the XRD pattern. Hence, to verify the existence of the carbon layer, the mapping of Co, S, C elements for the TEM image has been provided in **Figure 2**. A thin carbon layer with the thickness of around 16 nm was found to grow outside the cobalt sulfide uniformly, indicating the flexibility to prepare the well-established nanocomposite by simply adding the 1-dodecanethiol as both the carbon and sulfur sources during the synthesis of cobalt sulfide.

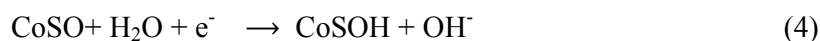
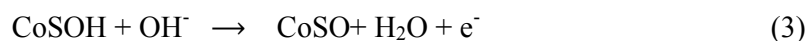
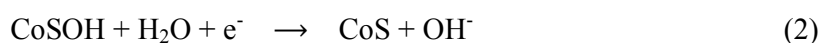
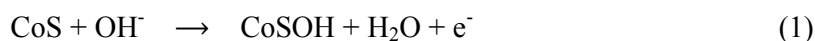
3.3 The electrochemical performance of the cobalt sulfide hydrangea macrophylla-based supercapacitor electrode

Furthermore, the electrochemical performance of the cobalt sulfide hydrangea macrophylla-based SC electrode was examined. The C_F value of the SC electrode with cobalt sulfide hydrangea macrophylla as the electroactive material was evaluated using the CV curves at a scan rate of 10 mV/s in the potential range of 0 to 0.4 V, and that for bare nickel foam was also measured for comparison, as shown in **Figure 3(a)**. The C_F value was calculated according to equation (1) as following.²⁵

$$C_F = \frac{\int I dV}{v \Delta V m} \quad (1)$$

where I is the current density, $\int I dV$ is the integrated area of the CV curve, v is the scan rate, ΔV is the potential window, and m is the weight of the active material in the electrode.

The pseudo-capacitance behaviors were observed for both of the case with a pair of the redox peaks. The area in the CV plot is found to be very small for the SC electrode composed of bare nickel foam, indicating the negligible capacitance for this case. Therefore, the contribution of the C_F value from the substrate, nickel foam, can be almost ignored for the cobalt sulfide hydrangea macrophylla-based SC electrode. A high C_F value of 324.17 F g^{-1} was obtained for the cobalt sulfide hydrangea macrophylla-based SC electrode. The peaks for the two pairs of oxidation and reduction reactions for the cobalt sulfide hydrangea macrophylla-based SC electrode were respectively indicated in the plots as shown in the following.²⁶



On the other hand, the GC/D plots for the SC electrodes with the cobalt sulfide hydrangea macrophylla on nickel foam and with bare nickel foam were measured at a current density of 0.5 A/g for the charging/discharging voltage from 0 to 0.4 V as shown in **Figure 3(b)**. The C_F value was calculated according to equation (2) as following.²⁵

$$C_F = \frac{I \Delta t}{m \Delta V} \quad (2)$$

where Δt is the discharge time and ΔV is the potential window during the charge/discharge

process. A longer charge/discharge time and a larger C_F value were achieved for the cobalt sulfide hydrangea macrophylla-based SC electrode. The first charge/discharge curve for the cobalt sulfide hydrangea macrophylla SC electrode can attain around 1200 s, but the case with bare nickel foam can only last the charge/discharge process for less than 100 s. A C_F value of 285 F/g was therefore obtained for the cobalt sulfide hydrangea macrophylla-based SC electrode. The phenomenon of the long charging time and short discharging time for the cobalt sulfide hydrangea macrophylla-based SC electrode is only observed for the first charge/discharge process, and the charging time reduces seriously after the first charge/discharge process. The long charging time on the first charge/discharge process is probably due to the inactivation of the electroactive material at the beginning of the measurement. In the first charge process the fixed current density was applied on the electrode and the charges were accumulated on the electrode while the redox reactions were occurred at the same time. Since the ions diffused and convected from the bulk electrolyte to the electrode continuously, the pore in the nanostructure may be expanded and therefore the electroactive material may be activated. Hence the charge and discharge durations become similar after the first charging process. Moreover, the Nyquist plots for the SC electrodes with the cobalt sulfide hydrangea macrophylla on nickel foam and with bare nickel foam were measured to investigate the conductivity and the interfacial resistance of the electroactive material and the electrolyte, as shown in **Figure 3(c)**, and the enlarged curves in the high frequency region as well as the equivalent circuit were inserted for more clearly observations.

The plot shows the responses of the frequency to the electrode/electrolyte system with the real component (Z') plotted against the imaginary component (Z'') of the impedance. Every point of data is at a diverse frequency with the upper right portion of the plot corresponding to the lower frequency.^{25,27} The x-intercept can be inferred to the equivalent series resistance (R_s) while the interfacial resistance between the electroactive material and the electrolyte (R_{ct}) can be estimated by the first semicircle fitted in the high frequency range. The similar R_s values of 0.60 and 0.63 Ω were respectively found for the SC electrodes with cobalt sulfide hydrangea macrophylla and bare nickel foam with the similar x-intercepts, indicating the conductivity is mainly influenced by the conductive metal substrate, the nickel foam. In addition, the Nyquist plot of the cobalt sulfide hydrangea macrophylla-based SC electrode exhibits a smaller semicircle over the high frequency range with the R_{ct} value of 0.40 Ω as compared with that for the SC electrode composed of only a bare nickel foam with the R_{ct} value of 2.25 Ω . The result can be attributed to the better performance of the SC electrode with the cobalt sulfide hydrangea macrophylla nanostructure which possesses high surface area for faradic reactions as well as the ion/electron accumulation and higher conductivity for charge transportation. Furthermore, **Figure 3(d)** demonstrates the reversibility of the cobalt sulfide hydrangea macrophylla-based SC electrode with its symmetric charge/discharge curves, except for the first charge/discharge process in which the material has not been activated. To further confirm the high specific surface area of the cobalt sulfide hydrangea macrophylla nanostructure, an aggregated nanostructure without any 2D nanopetals was

synthesized by reducing the vulcanized temperature from 230 to 190 °C for comparison. The nitrogen adsorption-desorption isotherms for these two nanostructures of cobalt sulfide were measured as shown in **Figure 4** to compare the specific surface area, in which the corresponding TEM images were also included. The specific surface areas were respectively estimated to be 0.15 and 1.38 m²/g for the aggregated and hydrangea macrophylla nanostructures. The nearly ten times higher specific surface area for the hydrangea macrophylla nanostructure than that for the aggregated forms strongly suggests that the large amount of active sites can be utilized to accumulate charges and precede faradic reactions for the former case.

3.4 The loading mass effect of the cobalt sulfide hydrangea macrophylla-based supercapacitor electrode

To further improve the electrochemical performance, the loading mass of the cobalt sulfide hydrangea macrophylla nanomaterial on the nickel foam was optimized for the SC electrode. **Figure 5** shows the CV curves of the SC electrode composed of 7.5, 10.0, 12.5, 15.0, and 17.5 mg cobalt sulfide hydrangea macrophylla nanostructures on the nickel foam. For the SC electrode with less amount of cobalt sulfide deposited on the nickel foam, *i.e.*, 7.5 and 10.0 mg on 1 cm² nickel foam, the redox peaks are hard to be observed, while the obvious peaks for the two pairs of redox reactions are found for the SC electrode with the loading mass higher than 12.5 mg. The highest C_F value of 324.17 F/g was achieved for the

SC electrode with 12.5 mg cobalt sulfides on the nickel foam, while 242.78, 298.80, 269.74, and 264.11 F/g were obtained for the SC electrodes with 7.5, 10.0, 15.0, and 17.5 mg cobalt sulfide on the nickel foam, respectively. Higher loading of the materials on the electrode may provide more sites for charge accumulation and faradic redox reactions. From this viewpoint, the more materials deposited on the electrode, the higher capacitance can be achieved for the pertinent SC electrode. However, too many materials on the electrode may cause aggregation of the cobalt sulfide and hence reduce the exposed surface area to the electrolyte, leading to the worse electrochemical performance for the corresponding SC electrode.

3.5 The fast charge–discharge ability and long-term stability tests

To further investigate the fast charge–discharge ability of the cobalt sulfide hydrangea macrophylla-based SC electrode, different scan rates of 5, 10, 25, 50 and 100 mV s⁻¹ were applied on measuring the CV curves as presented in **Figure 6**. The CV plots present similar shapes for the cases scanned at 5 and 10 mV/s, indicating the good capacitive behavior of the electrode in these conditions. For the higher scan rate, the shape of the CV plots only presents slightly distortion in the reduction region but distorted seriously in the oxidation region. Also, the slight increase on the peak separation was observed for the cases measured at higher scan rates. This phenomenon is common for the electrochemical measurement.²⁵ Last, the cycling performance of the cobalt sulfide hydrangea macrophylla-based SC electrode was investigated. **Figure 7** shows the GC/D plots measured for around 330,000 s of the repeated charge/discharge process using the cobalt sulfide hydrangea macrophylla-based SC electrode.

It can be clearly observed that the charge/discharge curve is very symmetric even when the measurement lasting for 330,000 s, indicating the good cycling stability of this SC electrode.

4. Conclusions

Self-synthesized cobalt sulfide hydrangea macrophylla was utilized as the electroactive material for the SC electrode. Several 2D cobalt sulfide nanopetals with thin carbon layers growing at the surrounding comprise the cobalt sulfide nanostructure by the growth mechanism of the initial nucleation, the dissolution for assembly growth, and finally the further growth to produce the hydrangea macrophylla architecture. By depositing 12.5 mg cobalt sulfide hydrangea macrophylla on the nickel foam as the SC electrode, a C_F value of 324.17 F/g was obtained at a scan rate of 10 mV/s. This good performance of the SC electrode with the cobalt sulfide hydrangea macrophylla is due to the large surface area for the ion/electron accumulation and faradic reactions as well as the high conductivity for charge transportation respectively benefited from the 2D nanopetals and the carbon layers. The fast charge–discharge ability and the good cycling stability of the SC electrode with the cobalt sulfides hydrangea macrophylla as the material were also confirmed by using the GC/D measurements.

Acknowledgements

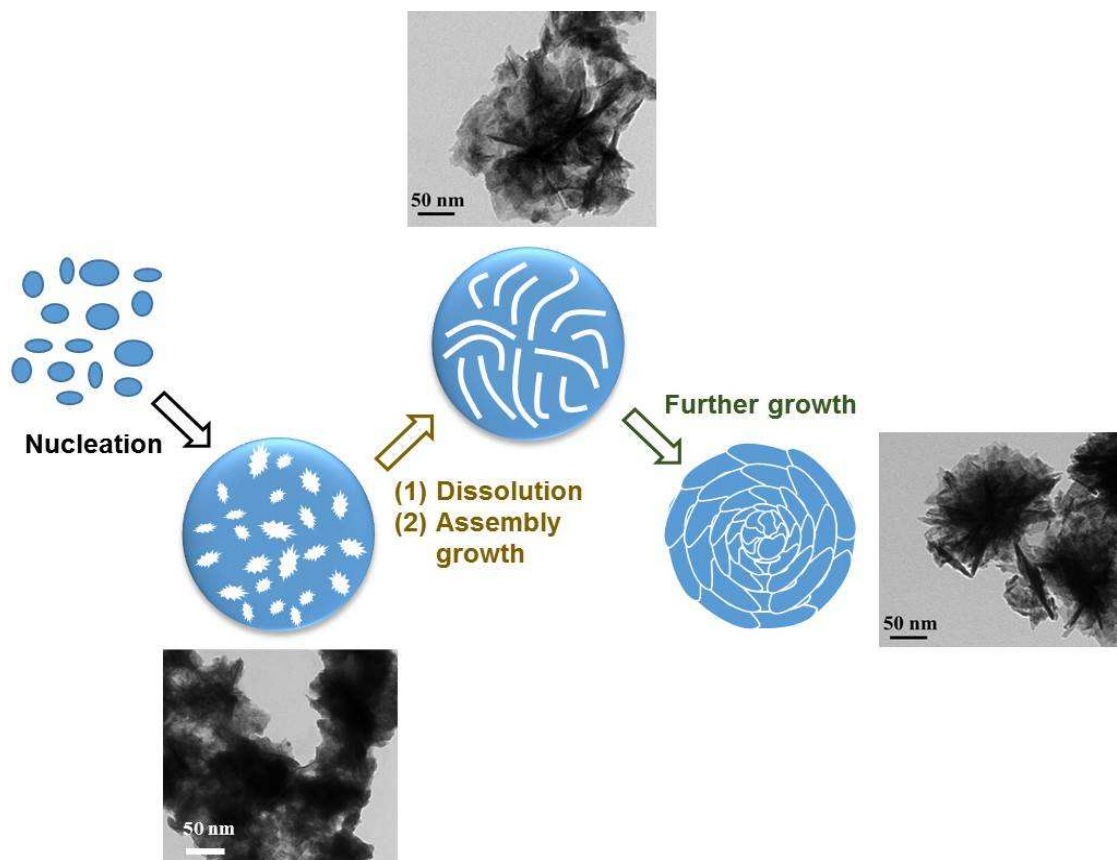
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Scheme 1 The illustration for the growth process of the cobalt sulfide hydrangea macrophylla.

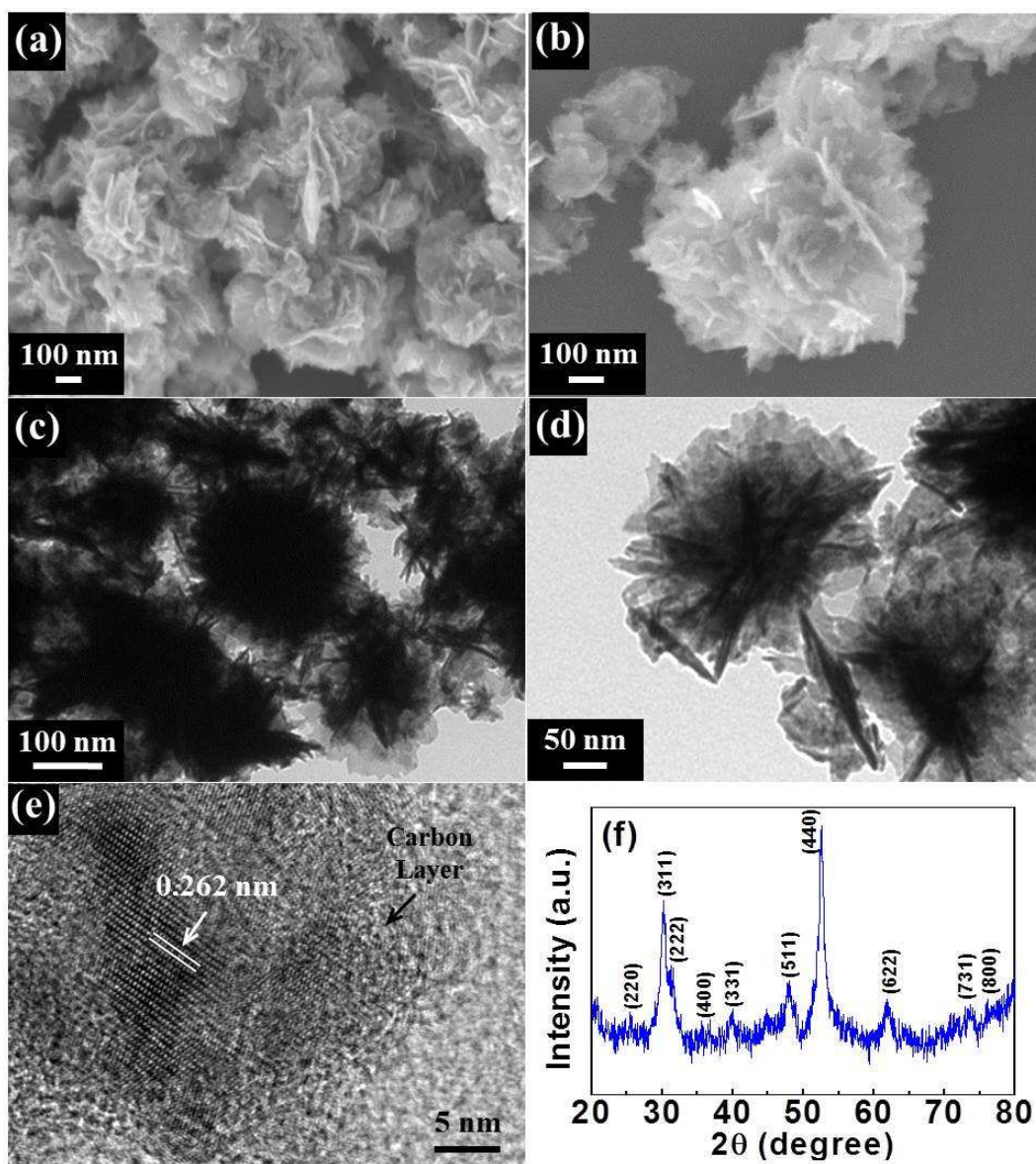


Figure 1 The SEM images at the (a) low magnification and (b) high magnification; the TEM images at the (c) low magnification and (d) high magnification; (e) the HRTEM image, and (f) the XRD pattern for the cobalt sulfide hydrangea macrophylla nanostructure.

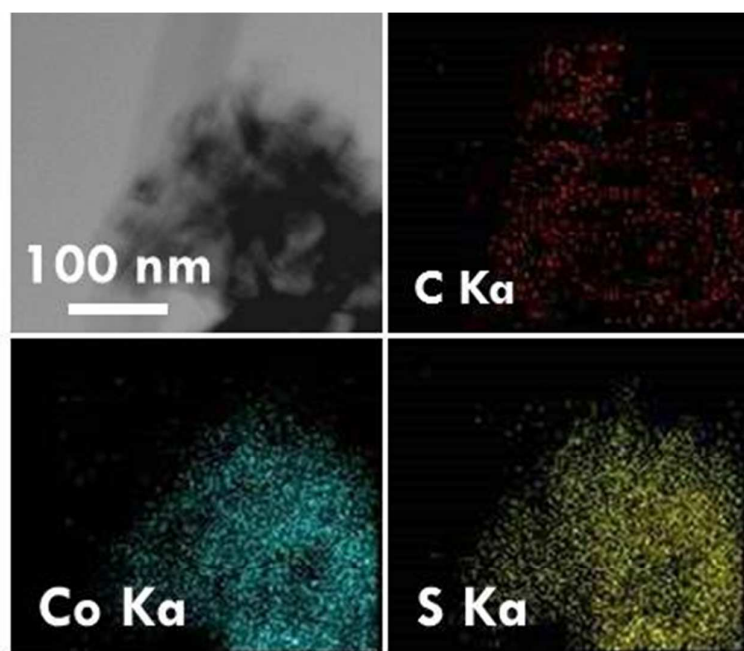


Figure 2 The TEM image and the EDS elemental mapping of C, Co, and S for the cobalt sulfide hydrangea macrophylla.

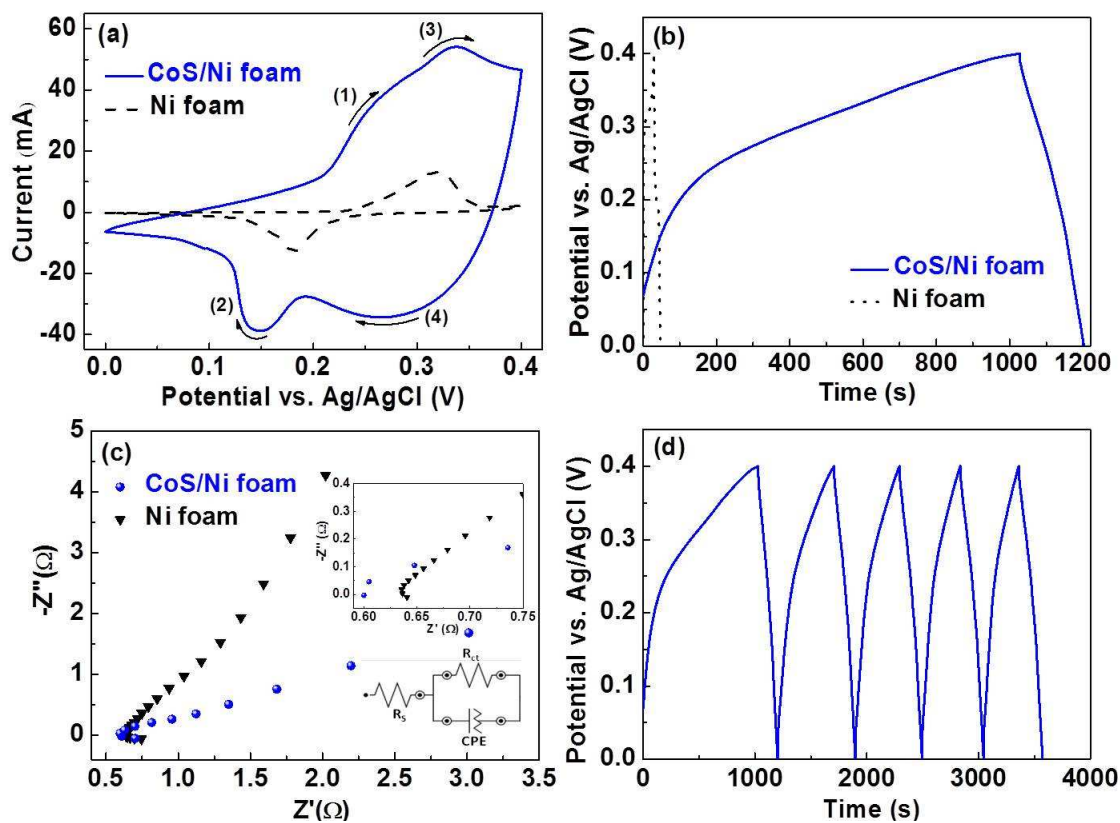


Figure 3 (a) The CV curves, (b) the GC/D plots, and (c) the Nyquist plots for the SC electrodes with the cobalt sulfide hydrangea macrophylla nanostructure on the nickel foam and the bare nickel foam, and (d) the GC/D plots of the first four charge/discharge curves for the SC electrode with the cobalt sulfide hydrangea macrophylla nanostructure on the nickel foam.

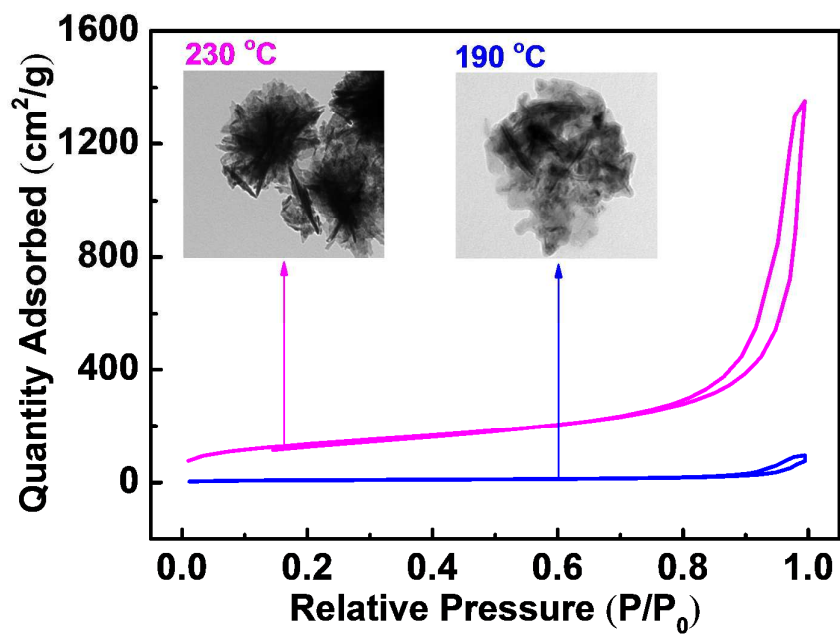


Figure 4 The N_2 adsorption–desorption isotherms of cobalt sulfides with the vulcanization temperature of 190 and 230 °C, and the corresponding TEM images were presented in the figure.

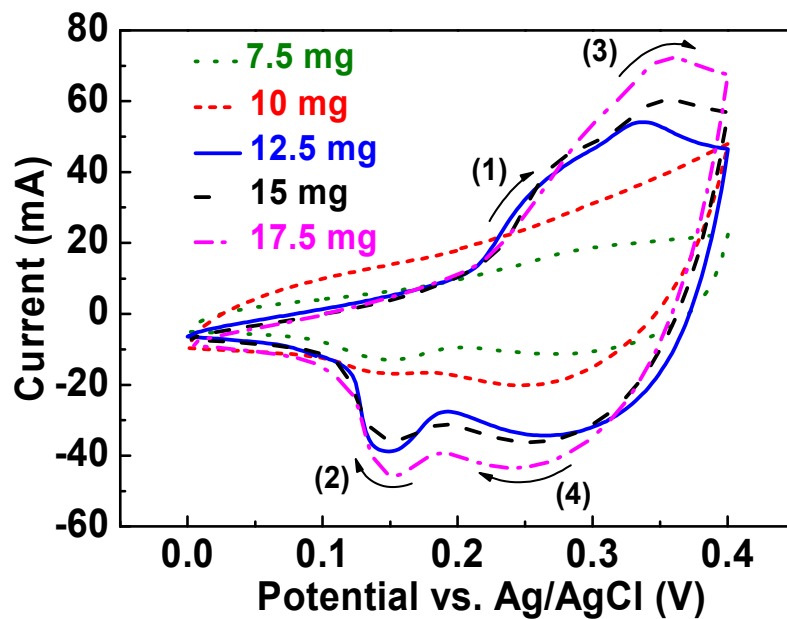


Figure 5 The CV curves for the SC electrodes with different loading masses of the cobalt sulfide hydrangea macrophylla nanostructure on the nickel foam.

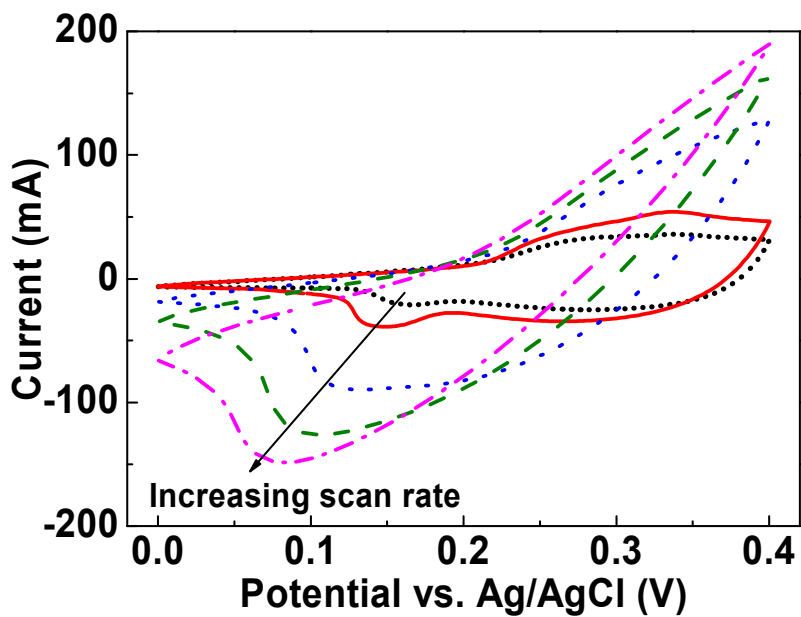


Figure 6 The CV curves for the SC electrodes with 12.5 mg cobalt sulfide hydrangea macrophylla nanostructure on the nickel foam measured at the scan rates of 5, 10, 25, 50, and 100 mV/s.

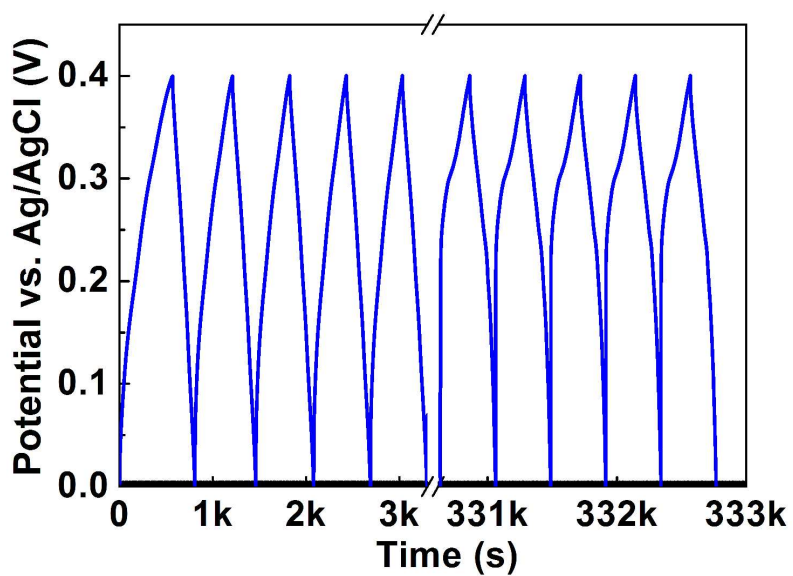


Figure 7 The GC/D plots measured by repeatedly charging and discharging for around 333,000 s for the SC electrodes with the cobalt sulfide hydrangea macrophylla nanostructure on the nickel foam.