


Article

# Highly Efficient Nanocarbon Coating Layer on the Nanostructured Copper Sulfide-Metal Organic Framework Derived Carbon for Advanced Sodium-Ion Battery Anode

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**Abstract:** High theoretical capacity and low-cost copper sulfide ( $\text{Cu}_x\text{S}$ )-based anodes have gained great attention for advanced sodium-ion batteries (SIBs). However, their practical application may be hindered due to their unstable cycling performance and problems with the dissolution of sodium sulfides ( $\text{Na}_x\text{S}$ ) into electrolyte. Here, we employed metal organic framework (MOF-199) as a sacrificial template to fabricate nanoporous  $\text{Cu}_x\text{S}$  with a large surface area embedded in the MOF-derived carbon network ( $\text{Cu}_x\text{S-C}$ ) through a two-step process of sulfurization and carbonization via  $\text{H}_2\text{S}$  gas-assisted plasma-enhanced chemical vapor deposition (PECVD) processing. Subsequently, we uniformly coated a nanocarbon layer on the  $\text{Cu}_{1.8}\text{S-C}$  through hydrothermal and subsequent annealing processes. The physico-chemical properties of the nanocarbon layer were revealed by the analytical techniques of high-resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDS), and scanning electron microscopy (SEM). We acquired a higher SIB performance (capacity retention (~93%) with a specific capacity of 372 mAh/g over 110 cycles) of the nanoporous  $\text{Cu}_{1.8}\text{S-C/C}$  core/shell anode materials than that of pure  $\text{Cu}_{1.8}\text{S-C}$ . This encouraging SIB performance is attributed to the key roles of a nanocarbon layer coated on the  $\text{Cu}_{1.8}\text{S-C}$  to accommodate the volume variation of the  $\text{Cu}_{1.8}\text{S-C}$  anode structure during cycling, enhance electrical conductivity and prevent the dissolution of  $\text{Na}_x\text{S}$  into the electrolyte. With these physico-chemical and electrochemical properties, we ensure that the  $\text{Cu}_{1.8}\text{S-C/C}$  structure will be a promising anode material for large-scale and advanced SIBs.

**Keywords:** copper sulfide ( $\text{Cu}_x\text{S}$ ); metal organic framework (MOF); sodium ion battery (SIB); carbon coating layer; nanoporous anode materials; high specific surface area; nanostructured anode;  $\text{H}_2\text{S}$  gas-assisted plasma-enhanced chemical vapor deposition (PECVD); sulfurization; carbonization

## 1. Introduction

Sodium ion batteries (SIBs) have drawn great attention as an alternative to lithium ion batteries (LIBs) for large-scale energy storage systems (ESS) such as home solar-power storage, microgrids, and load leveling, owing to the abundant resource and low cost of Na [1,2]. However, the Na<sup>+</sup> ion has a larger ionic radius of 1.06 Å and a heavier atomic weight of 23 g/mol relative to the 0.76 Å and 6.9 g/mol of the Li<sup>+</sup> ion [3]. These immutable properties have raised critical issues on sluggish Na<sup>+</sup> ion kinetics caused by Na<sup>+</sup>'s large migration energy barrier, thereby leading to the unsatisfactory electrochemical performance of electrode materials (e.g., graphite-based electrode) with the intercalation/deintercalation mechanism of the Na<sup>+</sup> ion.

As an alternative electrode material to overcome these bottlenecks, transition metal oxides (TMOs) [4] and sulfides (TMSs) [5] have been vigorously investigated as intercalation/conversion-type anode materials owing to their high theoretical capacity (400–560 mAh/g) [6]. Compared to TMO-based electrodes, TMS-based electrodes possess their own beneficial properties including their relatively small volume change, superior reversibility, and higher electrical conductivity because of proportionally- weaker M–S ionic bonds relative to their M–O counterparts, which enables enhanced rechargeable battery performance [7]. Among the TMS-based anode materials, cuprous sulfide (Cu<sub>x</sub>S) has been intensively investigated as a strong candidate electrode material for LIBs [8–17] and SIBs [3,7,18,19], owing to its unique properties of high theoretical capacity (~560 mAh/g for CuS and 337 mAh/g for Cu<sub>2</sub>S), low cost, the environmental harmlessness of sulfur, and good electrical conductivity (10<sup>−3</sup> S/cm) [7,20]. Although the Cu<sub>x</sub>S-based electrodes have been extensively studied, they have posed some major issues including [3,7,18,19]: (1) irreversible conversion reaction between Cu<sub>x</sub>S and the Li<sup>+</sup>/Na<sup>+</sup> ion, which induces a large volume variation of the Cu<sub>x</sub>S-based electrodes during prolonged cycling, bringing about corruption of structural integrity and capacity decay; (2) dissolution of sodium sulfide (Na<sub>x</sub>S) into electrolytes during cycling, causing the loss of active materials. The most viable approaches to overcome these limitations include nanostructure design and subsequent incorporation of nanocarbon (e.g., carbon nanotubes [21], reduced graphene oxide [9,22], and mesoporous carbon [8]) with Cu<sub>x</sub>S, electrolyte selection [23], and voltage range modification [3]. Metal organic frameworks (MOF) are a subclass of nanoporous coordination polymers composed of molecular building blocks comprising metal ions that are linked by organic linker ligands [24]. Because of MOF's appealing properties of crystallinity, along with its high surface area and porosity, these materials have been widely implemented into gas sorption/separation [25], toxic gas mitigation [26], catalysis [27], batteries, and supercapacitors [28,29]. Very recently, highly nanoporous MOFs were employed as a sacrificial template to synthesize Cu<sub>x</sub>S-carbon nanocomposite cathode materials through thermal evaporation of sulfur powders for LIBs [14,30]. Nevertheless, their cycling stability still needs to be improved [12] along with their specific capacity [28]. What remains largely unexplored to overcome these limitation is the design and fabrication of a Cu<sub>x</sub>S-MOF-derived carbon/nanocarbon (Cu<sub>x</sub>S-C/C) core/shell anode structure. In this structure, nanocarbon jointly surrounding the Cu<sub>x</sub>S-C could buffer against mechanical stresses derived from a large volume change of Cu<sub>x</sub>S during the sodiation-desodiation cycling process and mitigate a problem associated with structural pulverization of the Cu<sub>x</sub>S, thus enhancing the cycling performance. Furthermore, the nanocarbon is able to improve the electrical conductivity of the Cu<sub>x</sub>S and prevent the dissolution of Na<sub>x</sub>S into electrolytes during cycling.

Inspired by this, we embarked on designing and fabricating the nanoporous Cu<sub>x</sub>S-C network with a high surface area to incorporate a carbon nanolayer by producing a core-shell nanostructure through a two-step process. First, we synchronized sulfurization and carbonization via a H<sub>2</sub>S gas-assisted plasma-enhanced chemical vapor deposition (PECVD) process, in which it is possible for Cu<sup>2+</sup> ions in the core of a single MOF particle to be sulfurized at room temperature, thus forming CuS [25,26]. Furthermore, this process is more efficient when compared to solution processing for CuS microsphere synthesis [7]. Second, we coated the nanocarbon layer on the surface of the Cu<sub>x</sub>S-C. Furthermore, we applied the cut-off voltage range (0.01–3 V) for the battery test without compromising specific capacity, which differs from the previous report [3]. Digenite Cu<sub>1.8</sub>S-C (showing the highest capacity among the

polymorphs of  $\text{Cu}_x\text{S}$  investigated in this study) was coated by a nanocarbon layer to form a core/shell structure, demonstrating a specific capacity of 372 mAh/g at 2C over 110 cycles, superior to that of the pure  $\text{Cu}_{1.8}\text{S}$ -C anode, and a higher cycling stability with ~93% retention. Considering these results, we ensure that the highly nanoporous  $\text{Cu}_{1.8}\text{S}$ -C/C core/shell anode structure can shed light on resolving the remaining issues of  $\text{Cu}_x\text{S}$ -based anodes for large-scale, next-generation SIBs.

## 2. Materials and Methods

### 2.1. Synthesis of MOF-199

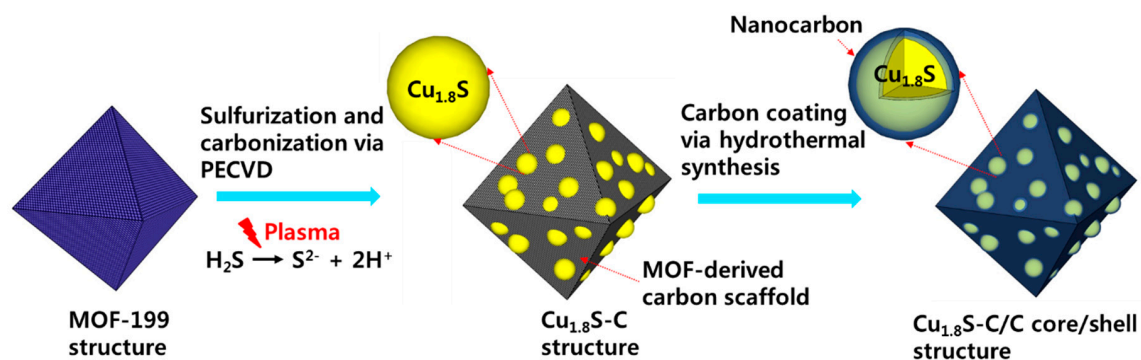
We fabricated metal organic framework (MOF-199) with an octahedral shape through a simple solvothermal synthesis method. In the typical synthesis,  $\text{Cu}_3(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Sigma-Aldrich, St. Louis, MI, USA) as a Cu-precursor (334.83 mg; 1.785 mmol), 1,3,5-benzenetricarboxylic acid (trimesic acid, H3BTC,  $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$ ) (Sigma-Aldrich) as an organic linker (196 mg; 0.933 mmol), and lauric acid (Fisher Scientific, Hampton, NH, USA) as a growth modulator of the MOF-199 structure (9.917 g; 49.5 mmol) were dissolved into n-butyl alcohol (70 mL) and then sonicated for 1 h to acquire a homogeneous solution using a sonicator with 40-kHz sound waves (Lab Companion; UC-10, JEIO TECH, Daejeon, Korea). The solution was subsequently transported into a 100-mL Teflon-lined stainless steel autoclave, which was pressurized at 140 °C for 5 h. After synthesis, we purified the as-synthesized MOF-199 particles via centrifugation with ethanol and deionized (DI) water several times. Finally, the purified MOF-199 particles were dried at 80 °C overnight in a drying oven. Figure S1 illustrates a dicopper (II) tetracarboxylate building block for MOF-199 [31].

### 2.2. Synthesis of $\text{Cu}_x\text{S}$ -MOF-Derived Carbon

Five hundred milligrams of MOF-199 were subjected to a two-step process of sulfurization and carbonization.  $\text{H}_2\text{S}$  (10%)/ $\text{N}_2$  (90%) mixture gas (30 sccm) and Ar gas (100 sccm) were flowed into a quartz tube in the PECVD system. Plasma power (100 W) was applied to decompose  $\text{H}_2\text{S}$  gas into atomic S and H, ions of  $\text{S}^{2-}$ ,  $\text{S}^-$ , and  $\text{H}^+$ , radical of  $\text{H}_2\text{S}^+$ , and molecular  $\text{H}_2$  at the temperature ranging from 350–650 °C at a rate of 5 °C/min [32]. Among these species, the  $\text{S}^{2-}$  radical was reacted with  $\text{Cu}^{2+}$  ions coordinated with the organic linker, forming nanostructured CuS even at room temperature [25,26]. The process pressure was retained as ~1.0 torr. During the sulfurization process, the original MOF-structure was dismantled through thermal decomposition and sulfurization of other elements (e.g., oxygen and hydrogen) in the original MOF unit structure, finally forming the nanocarbon network [14,33]. Further sulfurization and carbonization proceeded at the respective temperature (350, 550, and 650 °C) for 1 h. Finally, rapid cooling was carried out in an Ar gas environment at 100 standard cubic centimeter per minute (sccm).

### 2.3. Synthesis of $\text{Cu}_{1.8}\text{S}$ -MOF-Derived Carbon/Carbon Core/Shell Structure

$\text{Cu}_{1.8}\text{S}$  (77 wt%)-MOF-derived carbon (23 wt%) sulfurized at 550 °C (200 mg; 1.1 mmol) and dextrose (Sigma-Aldrich) (400 mg; 2.2 mmol) were dissolved into 12.5 mL of de-ionized (DI) water. Following this, the solution was sonicated for 30 min for homogeneous mixing. Subsequently, the solution was put into a 25-mL Teflon-lined autoclave for hydrothermal synthesis at 190 °C for 12 h. After completing the hydrothermal synthesis, the resulting powder sample was purified through centrifugation with DI water several times. Finally, the purified powder sample was subjected to the annealing process at 500 °C for 8 h under a  $\text{Ar}/\text{H}_2$  (90/10 wt%) mixture gas environment. Figure 1 schematically illustrates each synthesis procedure for the  $\text{Cu}_{1.8}\text{S}$ -C/C core/shell structure.



**Figure 1.** The schematic diagram representing each synthesis process for the  $\text{Cu}_{1.8}\text{S-C/C}$  core/shell structure.

#### 2.4. Structural Analysis of $\text{Cu}_x\text{S-C/C}$

The phase identification of the MOF-199 and  $\text{Cu}_x\text{S-C}$  was acquired by X-ray diffraction (XRD) (Bruker, Billerica, MA, USA; D8 ADVANCE). The morphology and structural features were observed using scanning electron microscopy (SEM) (JEOL, Akishima, Japan; JSM-7600F) and Cs corrected S/transmission electron microscopy (TEM) (JEOL, Akishima, Japan; JEM-ARM200F). The quality of nanocarbon in the  $\text{Cu}_{1.8}\text{S-C/C}$  core/shell structure was measured by Raman spectroscopy (NT-MDT, Moscow, Russia; Ntegra Spectra DUO Max). Additionally, the thermal behavior of the MOF-199 and  $\text{Cu}_x\text{S-C}$  samples and the weight contents of the  $\text{Cu}_x\text{S}$  in each  $\text{Cu}_x\text{S-C}$  sample were measured by using thermogravimetry (TG)-differential thermal analysis (DTA) (SEICO INST, Chiba, Japan; TG/DTA7300). The specific surface area and pore volume of the MOF-199 and  $\text{Cu}_{1.8}\text{S-C/C}$  were measured by using Brunauer-Emmett-Teller (BET) equipment (Micromeritics, Norcross, GA, USA; ASAP2020). Micropore and meso-/macro-pore size distributions were evaluated through the Horvath-Kawazoe (HK) and Barrett-Joyner-Halenda (BJH) methods, respectively. The chemical composition, electronic states and purity of the  $\text{Cu}_{1.8}\text{S-C/C}$  sample were analyzed by using X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, Waltham, MA, USA; K-alpha).

#### 2.5. Sodium Ion Battery Performance of $\text{Cu}_x\text{S-C}$ and $\text{Cu}_{1.8}\text{S-C/C}$ Anode Structures

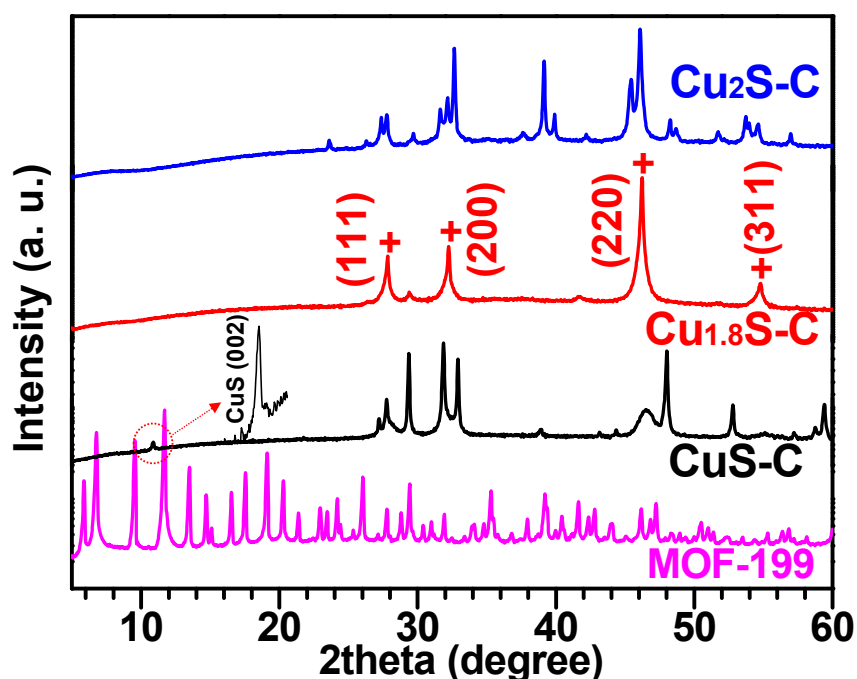
The electrode slurry was fabricated by mixing active materials (80 wt%), graphene nanoplatelets with a surface area of  $500 \text{ m}^2/\text{g}$  (Sigma-Aldrich) (10 wt%) as a conducting agent, and polyvinylidene difluoride (PVDF) (Sigma-Aldrich) (10 wt%) as a binder in the solvent of *n*-methyl-2-pyrrolidone (Sigma-Aldrich). The slurry was coated onto a copper current collector and then dried at  $80 \text{ }^\circ\text{C}$  in a drying oven for 12 h. The coin-type of cells composed of the  $\text{Cu}_x\text{S-C}$  and  $\text{Cu}_{1.8}\text{S-C/C}$  as the working electrodes were assembled with cell components (Welcos, Seoul, Korea) in a glove box under an inert Ar gas environment. Coin-cells were assembled with a porous glass fiber (grade GF/F, Whatman, Little Chalfont, UK) film as a separator, 1 M sodium trifluoromethanesulfonate ( $\text{NaSO}_3\text{CF}_3$ ) (Sigma-Aldrich) in diethylene glycol dimethyl ether (DEGDME) (Sigma-Aldrich) as an electrolyte, and a sodium (Sigma-Aldrich) foil electrode as counter and reference electrodes. The galvanostatic charge and discharge cycling test was carried out by using a multichannel battery testing unit (CTS-Lab, Asselfingen, Germany; BaSyTec). The cyclic voltammetry (CV) for the  $\text{Cu}_{1.8}\text{S-C/C}$  anode sample was conducted using a multi-channel potentiostat (Bio Logic, Seyssinet-Pariset, France; VMP3) in the voltage range of 0.01–3.0 V (vs.  $\text{Na}^+/\text{Na}$ ) at a scan rate of  $0.2 \text{ mV/s}$ .

### 3. Results and Discussion

#### 3.1. Structural and Morphological Properties of MOF-199, $\text{Cu}_x\text{S-C}$ and $\text{Cu}_{1.8}\text{S-C/C}$ Core/Shell Structures

Figure 2 shows the XRD patterns of the MOF-199 and three different  $\text{Cu}_x\text{S}$  samples. The peaks of XRD for the samples subjected to the different sulfurization conditions were consistent with the hexagonal covellite  $\text{CuS}$  (PDF#06-0464) at  $350 \text{ }^\circ\text{C}$ , digenite  $\text{Cu}_{1.8}\text{S}$  (PDF#47-1748) at  $550 \text{ }^\circ\text{C}$  and chalcocite

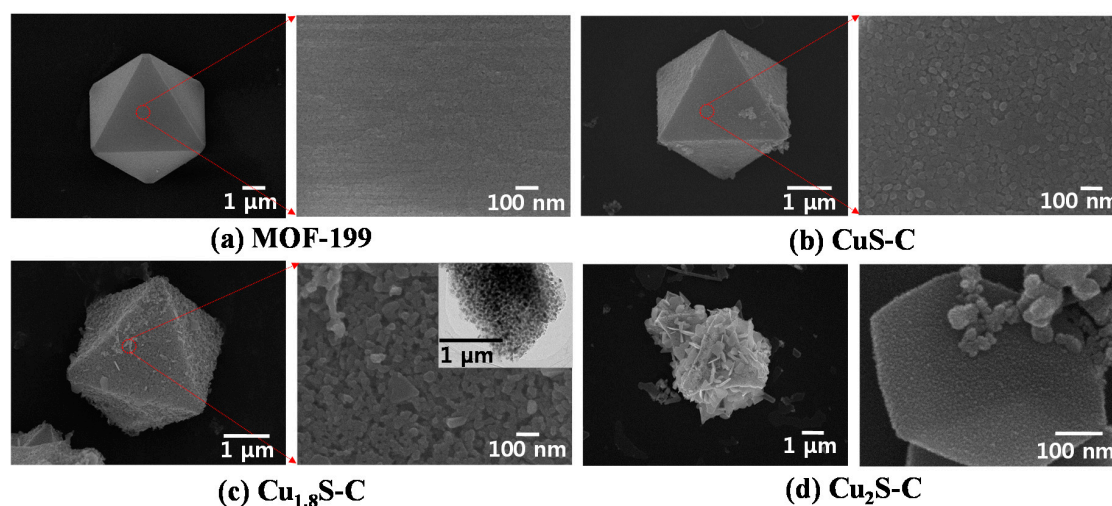
$\text{Cu}_2\text{S}$  (PDF#84-1770) at 650 °C, respectively. There was no other peak regarding MOF-199, sulfur,  $\text{Cu}_2\text{O}$ , and impurities after the two-step process of sulfurization and carbonization, highlighting that the as-synthesized MOF-199 was completely transformed into the copper sulfide ( $\text{Cu}_x\text{S}$ ) that was incorporated in the MOF-derived carbon network. Noticeably, the vaporization degree of sulfur proportionally increased with sulfurization temperature from 350–650 °C, thus transforming the copper-poor ( $\text{CuS}$ ) to the copper-rich ( $\text{Cu}_{1.8}\text{S}$  and  $\text{Cu}_2\text{S}$ ) phases with temperature [20]. For the cubic structure of  $\text{Cu}_{1.8}\text{S}$ , we could identify refined lattice constants ( $a = b = c = 5.55 \text{ \AA}$ ) according to Bragg's law, similar to the reported value of  $\text{Cu}_{1.8}\text{S}$  [3]. We observed no peak corresponding to the carbon in the  $\text{Cu}_x\text{S}$ -C samples, which is probably due to the screening effect induced by the  $\text{Cu}_x\text{S}$ . Alternatively, we proved the presence of the carbon by using EDS elemental mapping and spectra data (Figures S2–S4).



**Figure 2.** XRD patterns of the MOF-199 and three different samples of  $\text{Cu}_x\text{S}$ . Note that intensity is in logarithmic scale. We assign the (002) reflection at  $\sim 10^\circ$  in the  $\text{CuS}$ -C sample as “ $\text{CuS}$  (002)”.

Figure 3a demonstrates the SEM images showing the morphologies of as-synthesized MOF-199 with an octahedral shape used as a sacrificial template for  $\text{Cu}_x\text{S}$  embedded in a conductive nanocarbon scaffold. EDS mapping and spectra results of the as-synthesized MOF-199 structure proved that the constituent elements (e.g., Cu, O, and C) were uniformly distributed in the entire region of the structure (see Figure S5). SEM images presented in Figure 3b–d demonstrate the morphological variations of the  $\text{Cu}_x\text{S}$  with the sulfurization temperature from 350–650 °C. We can observe a larger number of  $\text{Cu}_x\text{S}$  nanoplates protruding from the surface at higher temperature, thus confirming that the degree of  $\text{Cu}_x\text{S}$  growth was proportionally increased with the sulfurization temperature. The high magnification SEM image of Figure 3c exemplifies the uniformly-distributed interconnected/aggregated  $\text{Cu}_{1.8}\text{S}$  nanoparticles in the carbon network. The inset TEM image in Figure 3c identifies the average size ( $\sim 60 \text{ nm}$ ) of  $\text{Cu}_{1.8}\text{S}$  nanoparticles, which is consistent with the nanoparticle distribution presented in Figure 3c. At 650 °C, the intensive sulfurization process increased the growth rate of  $\text{Cu}_2\text{S}$  nanoflakes, hence causing the collapse of an overall octahedrally-shaped structure as exhibited in the higher magnification SEM image in Figure 3d.

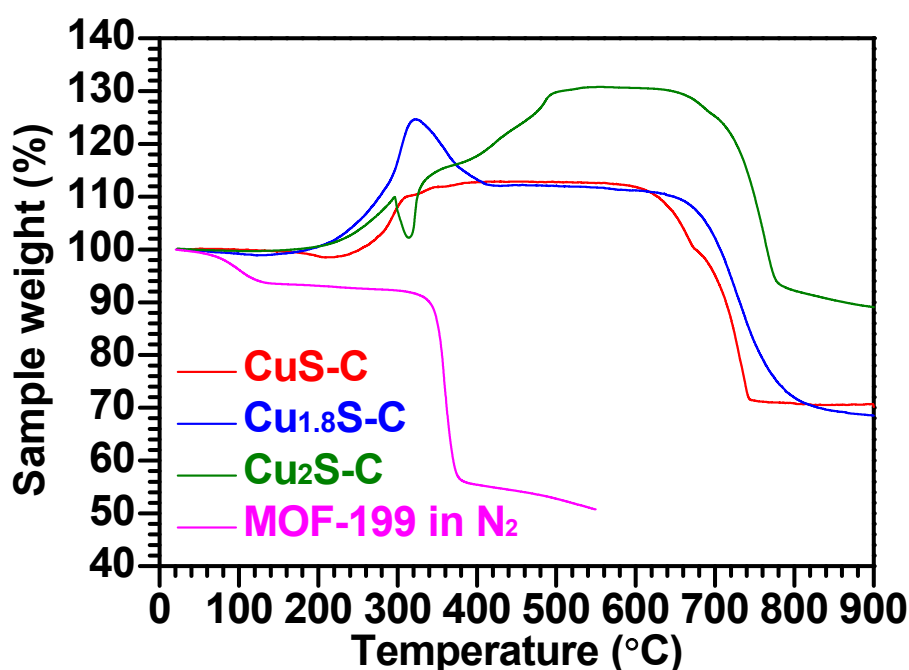




**Figure 3.** SEM images showing the morphological characteristics of as-synthesized MOF-199 and the degree increment of  $\text{Cu}_x\text{S}$  samples and their corresponding morphological variation with sulfurization and carbonization temperature through the  $\text{H}_2\text{S}$  gas-assisted PECVD process. (a) MOF-199; (b) CuS-C at 350 °C; (c)  $\text{Cu}_{1.8}\text{S-C}$  at 550 °C; (d)  $\text{Cu}_2\text{S-C}$  at 650 °C.

### 3.2. Thermogravimetric Analysis of MOF-199 and $\text{Cu}_x\text{S-C}$ Structures

Figure 4 demonstrates the thermal behavior of the MOF-199 and  $\text{Cu}_x\text{S-C}$  in the temperature ranging from 20–900 °C. The MOF-199 was thermally degraded under an inert nitrogen ( $\text{N}_2$ ) gas environment, hence resulting in a weight decrease (~36%) at around 350 °C according to the TG curve. This weight loss is attributed to the decomposition of organic linker ( $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$ ), which occurred around 300 °C. The three  $\text{Cu}_x\text{S-C}$  samples were subjected to the TG analysis in an air atmosphere to identify the contents of  $\text{Cu}_x\text{S}$  in each  $\text{Cu}_x\text{S-C}$  sample. Figure 4 shows the three different  $\text{Cu}_x\text{S}$  polymorphs undergoing the multi-step reactions with oxygen in air in the temperature ranging from 20–900 °C. The detailed reaction mechanism is presented in the Supplementary Information [14]. Based on the mechanism, we can calculate the real contents of CuS,  $\text{Cu}_{1.8}\text{S}$ , and  $\text{Cu}_2\text{S}$  in each  $\text{Cu}_x\text{S-C}$  structure as ~46, ~77, and ~91 wt%, respectively.



**Figure 4.** TG curves of CuS-C,  $\text{Cu}_{1.8}\text{S-C}$ , and  $\text{Cu}_2\text{S-C}$  in air and MOF-199 in a  $\text{N}_2$  gas environment.

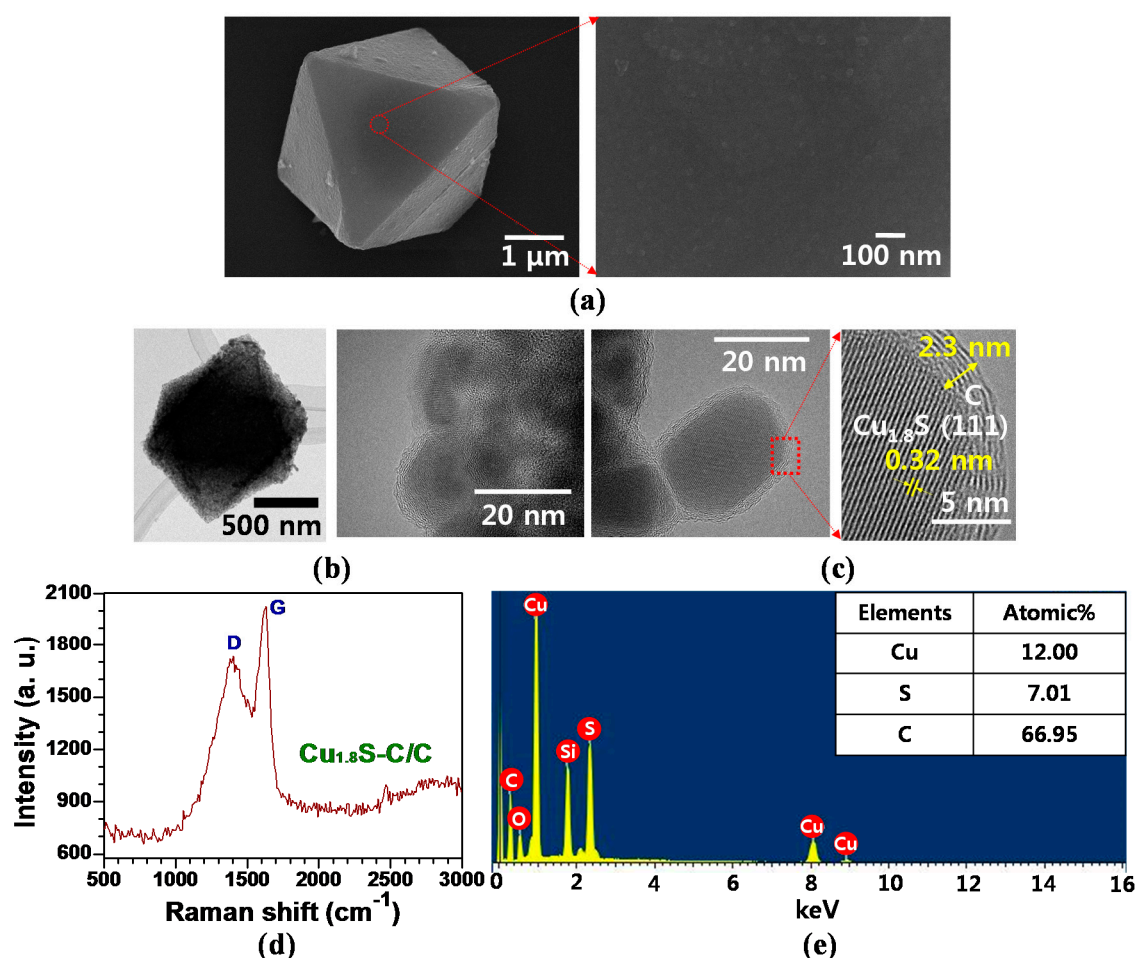
### 3.3. Structural and Morphological Properties of $\text{Cu}_{1.8}\text{S-C/C}$ Core/Shell Structures

The MOF-derived carbon networks play an important role in enhancing the electrical conductivity of  $\text{Cu}_x\text{S-C}$  samples and buffering against structural variation during charge and discharge cycles. Figure 5a reveals the characteristic surface of  $\text{Cu}_{1.8}\text{S-C}$  with the glucose-based carbon coating layer. Compared to the  $\text{Cu}_{1.8}\text{S-C}$  without carbon coating (Figure 3c), the individual morphologies of  $\text{Cu}_{1.8}\text{S}$  nanoparticles were less distinguishable since the nanocarbon layer was coated on the surface, and then, the nanoporous regions among them were effectively filled with the coated carbon. The TEM images in Figure 5b highlight a single  $\text{Cu}_{1.8}\text{S-C/C}$  core-shell structure (lower magnification image) and  $\text{Cu}_{1.8}\text{S}$  nanoparticles embedded in the carbon network (higher magnification image). We can distinguish between  $\text{Cu}_{1.8}\text{S}$  nanoparticles and low-degree graphitic carbon by the contrast difference (the brighter region corresponds to the carbon, whereas the darker region the  $\text{Cu}_{1.8}\text{S}$ ), which is consistent with the TEM image shown in the inset of Figure 3c. Figure 5c more clearly shows the  $\text{Cu}_{1.8}\text{S-C/C}$  core-shell structure. The high resolution TEM image helps us to measure the interlayer distance ( $\sim 0.32$  nm) of the  $\text{Cu}_{1.8}\text{S}$  (111) plane in the core-region and the thickness ( $\sim 2.3$  nm) of the carbon coating layer in the shell-region. Figure S6 displays an HRTEM image showing the interlayer distance ( $\sim 0.27$  nm) of the  $\text{Cu}_{1.8}\text{S}$  (200) plane and the thickness ( $\sim 2.6$  nm) of the carbon layer. Figure S7 illustrates the EDS line scanning results of a  $\text{Cu}_{1.8}\text{S-C/C}$  core-shell structure to identify the distribution of S and C elements comprising the structure. Note that the results of elemental Cu have low reliability due to the noise-inducing effects of the Cu grid on the detection of accurate results. Raman spectra results exhibited the presence of the carbon layer coated on the  $\text{Cu}_{1.8}\text{S-C/C}$  core-shell structure according to the typical G- and D-band peaks appearing at  $\sim 1580$  and  $\sim 1350$   $\text{cm}^{-1}$  (Figure 5d). Their peak ratio ( $I_D/I_G$ ) reached to  $\sim 0.85$ , which indicates low-degree graphitic carbon [34]. The visible inner carbon structure is attributed to the organic linker decomposition, whereas the external carbon structure to the conversion from glucose to the amorphous carbon through the hydrothermal synthesis and subsequent annealing process. For comparison purposes, we calculated the  $I_D/I_G$  peak ratio ( $\sim 0.93$ ) of the MOF-derived inner carbon of the  $\text{Cu}_{1.8}\text{S-C}$  sample (Figure S8); this value is comparable to that of the  $\text{Cu}_{1.8}\text{S-C/C}$  sample comprising both glucose-derived external and MOF-derived inner carbons. These results suggest that both external and inner carbons belong to the low-degree graphitic carbon without significant structural distinctions between them. The EDS spectra in Figure 5e exhibit the presence of each element (Cu, S, and C) comprising the  $\text{Cu}_{1.8}\text{S-C/C}$  core/shell particle sample. Note that Si and O peaks are related to the  $\text{Si/SiO}_x$  substrate used for SEM image acquisition of the particles. The atomic ratio of Cu to S is measured as  $\sim 1.7$ , which is close to the ratio of  $\text{Cu}_{1.8}\text{S}$ .

### 3.4. Surface Area and Porosity of MOF-199 and $\text{Cu}_{1.8}\text{S-C/C}$ Core/Shell Structures

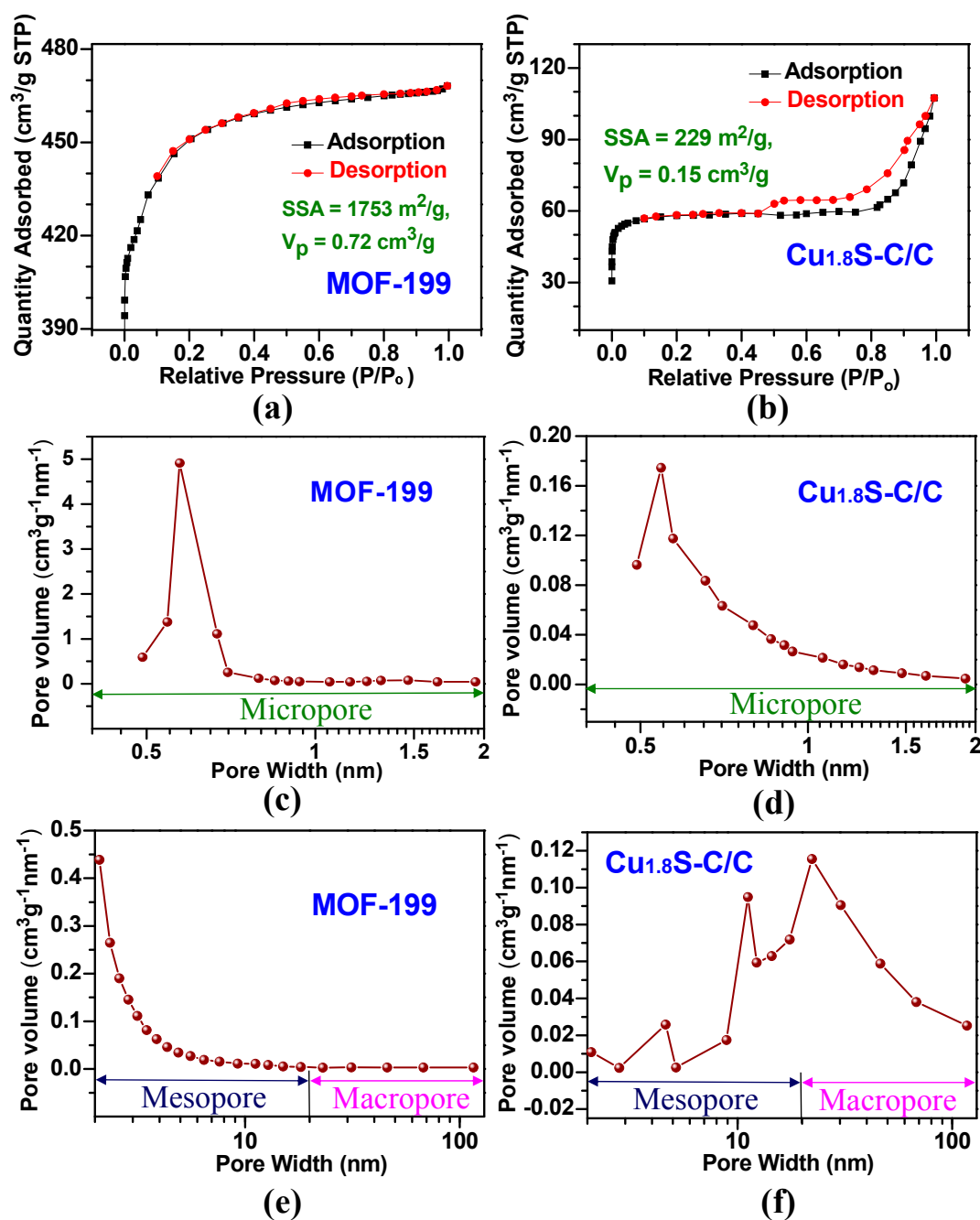
The large surface area and porosity of  $\text{Cu}_{1.8}\text{S-C/C}$  could promote sodium ion diffusion in the structure and increase the available sites for sodium ion accommodation during the charge and discharge cycle, thereby enhancing SIB performance [30]. To prove the correlation between high porosity and the large surface area of the  $\text{Cu}_{1.8}\text{S-C/C}$  and its electrochemical performance, we analyzed the  $\text{N}_2$  adsorption and desorption isotherms and pore-size distribution curves of the MOF-199 and  $\text{Cu}_{1.8}\text{S-C/C}$ , respectively (see Figure 6). The MOF-199 sample illustrated a typical type-I isotherm defined by IUPAC (International Union of Pure and Applied Chemistry) as the steep rise of the uptake occurred at low  $\text{N}_2$  relative pressure. This is because of the filling of  $\text{N}_2$  in the micropores followed by a plateau region, which is representative of a microporous material (Figure 6a) [35]. Conversely, the  $\text{Cu}_{1.8}\text{S-C/C}$  sample exhibited an isotherm with a type-H3 hysteresis loop, according to the IUPAC definition, due to the low volume ( $\sim 59$   $\text{cm}^3/\text{g}$  at standard temperature and pressure (STP)) adsorbed at low relative pressure ( $P/P_0 < 0.45$ ). This result could be attributed to the low specific surface area ( $229$   $\text{m}^2/\text{g}$ ) and pore volume ( $0.15$   $\text{cm}^3/\text{g}$ ). Furthermore, the isotherm of the  $\text{Cu}_{1.8}\text{S-C/C}$  sample showed an additional adsorption volume of  $\text{N}_2$  gas at the higher relative pressure level ( $P/P_0 > 0.5$ ) (Figure 6b) as the  $\text{Cu}_{1.8}\text{S-C/C}$  sample had broad distributions of slit-shaped meso-/macro-pores with a pore volume of  $0.08$   $\text{cm}^3/\text{g}$ , thus supporting the type-H3 hysteresis loop (Figure 6f) [36]. The MOF-199 exhibited a

sharp peak with a maximum at 0.57 nm showing a micropore volume ( $0.61 \text{ cm}^3/\text{g}$ ) in the micropore range (Figure 6c), whereas the  $\text{Cu}_{1.8}\text{S-C/C}$  a (slightly shifted) maximum peak at 0.54 nm (Figure 6d), suggesting that the micropores (pore volume:  $0.07 \text{ cm}^3/\text{g}$ ) of the  $\text{Cu}_{1.8}\text{S-C/C}$  were retained after the sulfurization and carbonization process. Furthermore, the MOF-199 showed a broad peak in the range of 2–10 nm, indicating the presence of mesopores (pore volume:  $0.11 \text{ cm}^3/\text{g}$ ) in the structure (Figure 6e). Furthermore, the specific surface areas of the MOF-199 and  $\text{Cu}_{1.8}\text{S-C/C}$  samples were measured as 1753 ( $1517$  (micropore) +  $236$  (meso-/macropore)) and 229 ( $206$  (micropore) +  $23$  (meso-/macropore))  $\text{m}^2/\text{g}$ , respectively. The decrease in the pore volume and specific surface area of the  $\text{Cu}_{1.8}\text{S-C/C}$  stems from the microstructural variation occurring during the sulfurization and carbonization process. Despite this, the  $\text{Cu}_{1.8}\text{S-C/C}$  somewhat retained the MOF-199-derived micropores and the newly-generated mesopores. It should be noted that the  $\text{Cu}_{1.8}\text{S-C/C}$  had a higher pore volume and specific surface area compared to the previous reports of  $\text{Cu}_x\text{S-C/C}$  [20,30,33]. These results suggest that the  $\text{Cu}_{1.8}\text{S-C/C}$  could offer facilitated  $\text{Na}^+$  ion diffusion and reaction, inter-space volume to accommodate volume change, and a large contact area of the electrode/electrolyte interface during cycling process, thus leading to enhanced SIB performance [18].



**Figure 5.** (a) High and low magnification SEM images showing the morphological features of the  $\text{Cu}_{1.8}\text{S-C/C}$  core/shell structure; (b) TEM images of an octahedral  $\text{Cu}_{1.8}\text{S-C/C}$  sample; (c) high resolution TEM (HR-TEM) pictures to reveal the core/shell structure of the  $\text{Cu}_{1.8}\text{S-C/C}$  sample, along with the interlayer distance of the  $\text{Cu}_{1.8}\text{S}$  (111) plane and the zoom-in image of the glucose-based carbon coating layer, denoted as C; (d) Raman and (e) EDS spectra of the  $\text{Cu}_{1.8}\text{S-C/C}$  sample.



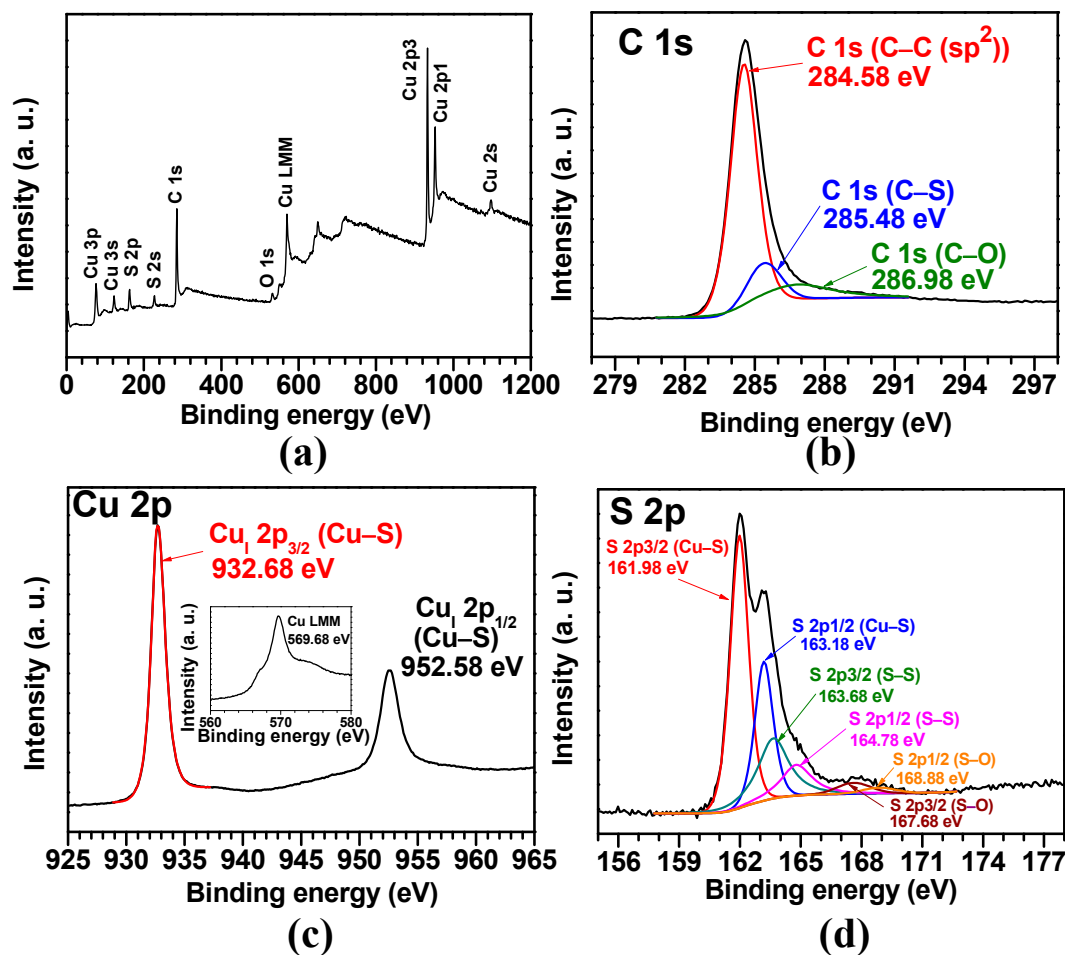


**Figure 6.** (a,b) Nitrogen adsorption–desorption isotherms of the MOF-199 and  $\text{Cu}_{1.8}\text{S-C/C}$  structures; (c–f) pore size distribution curves of the MOF-199 and  $\text{Cu}_{1.8}\text{S-C/C}$  structures. Note that pore width is in logarithmic scale.

### 3.5. X-ray Photoelectron Spectroscopy Analysis of $\text{Cu}_{1.8}\text{S-C/C}$ Core/Shell Structure

To study the chemical composition, electronic state, and purity of the  $\text{Cu}_{1.8}\text{S-C/C}$  sample, we conducted XPS analysis. Figure 7a demonstrates a wide-scan XPS spectra, proving the presence of Cu, S, C, and O elements with their characteristic binding energies calibrated by referencing C 1s  $\text{sp}^2$  bonding (284.58 eV shown in Figure 7b). Figure 7c exhibits the two strong peaks at 932.68 and 952.58 eV, associated with  $\text{Cu}_{(I)} 2p_{3/2}$  and  $\text{Cu}_{(I)} 2p_{1/2}$ , respectively, and there exists no satellite peak related to  $\text{Cu}^{2+}$ , thus proving only  $\text{Cu}^+$  exists in the  $\text{Cu}_{1.8}\text{S}$  [37]. The inset of Figure 7c presents the Cu LMM Auger transition with a maximum peak at 569.68 eV, which is the typical binding energy value for  $\text{Cu}_{1.8}\text{S}$  [38]. Figure 7d shows S 2p spectra, completed by data fitting, with a characteristic

S 2p doublet for  $S^{2-}$  with S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> peaks appearing at 161.98 and 163.18 eV, respectively [39]. The binding energy (161.98 eV) of S 2p<sub>3/2</sub> could correspond to S atoms bonded to Cu (S–Cu), forming Cu<sub>1.8</sub>S. The shoulder peaks appearing at 163.68 and 164.78 eV are related to S atoms in S–S bonds [38]. The binding energy peaks at 167.68 and 168.88 eV can be due to SO<sub>4</sub><sup>2-</sup> groups [40] formed by surface oxidation during the sulfurization process. No other impurity peak was observed, suggesting the Cu<sub>1.8</sub>S-C/C sample was relatively pure.

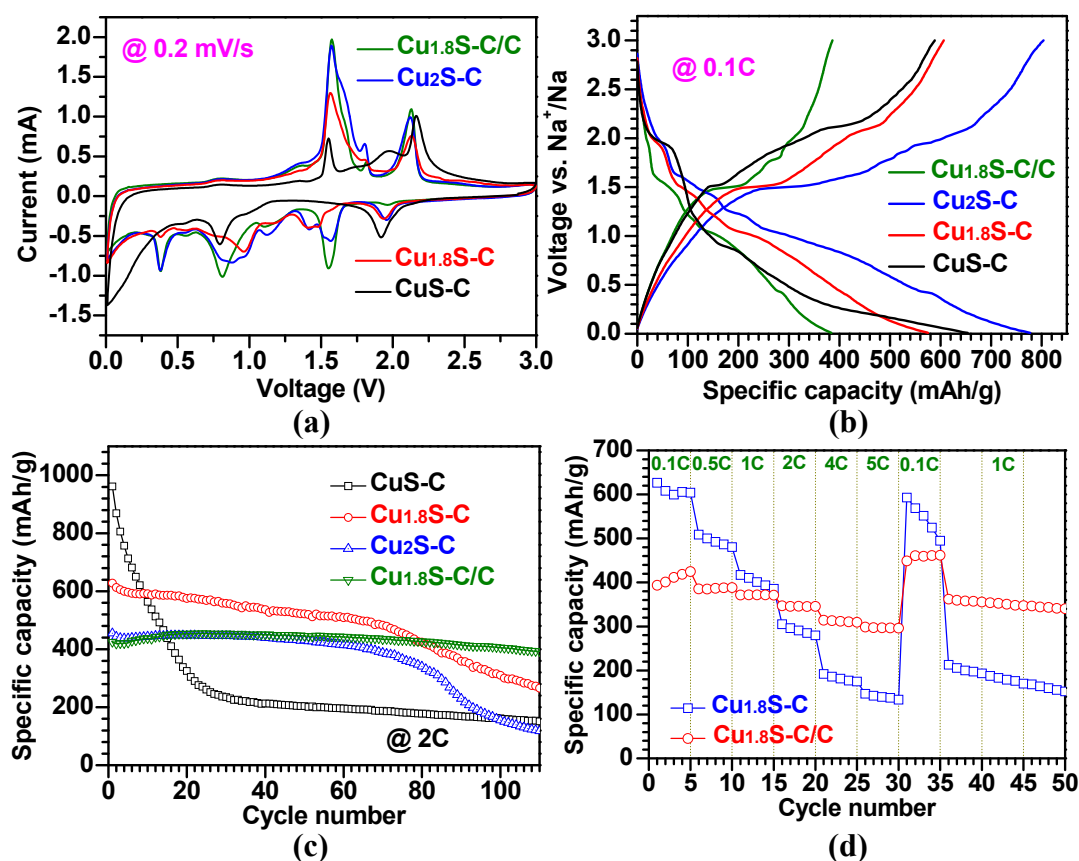


**Figure 7.** XPS spectra of the Cu<sub>1.8</sub>S-C/C: (a) survey spectra; high-resolution spectra of (b) C 1s, (c) Cu 2p, and (d) S 2p.

### 3.6. Electrochemical Performance of Cu<sub>x</sub>S-C and Cu<sub>1.8</sub>S-C/C Core/Shell Structures

Figure 8 demonstrates the SIB performance of Cu<sub>x</sub>S-C and Cu<sub>1.8</sub>S-C/C structures with the aforementioned physico-chemical properties. Figure 8a shows the cyclic voltammetry (CV) curves for the Cu<sub>x</sub>S-C and Cu<sub>1.8</sub>S-C/C anode samples for the second charge-discharge cycle. For all the samples, the two main oxidation (anodic) peaks occurred at ~1.6, and ~2.1 V, while the three main reduction (cathodic) peaks appeared at ~0.8, ~1.5, and ~1.9 V. These redox peaks, in conjunction with the other peaks, are associated with the multi-step electrochemical reactions for sodiation/desodiation process. Furthermore, these peaks correspond to the plateaus shown in the voltage profile curves of the same sample (Figure 8b), consistent with the previous reports of Cu<sub>x</sub>S-based anodes [3,7,18,19]. In Figure 8c, cycling performance results of the Cu<sub>1.8</sub>S-C/C sample demonstrate that the specific capacity increased from 402 to 426 mAh/g for the initial 20 cycles due to its microstructural changes [16], which can offer additional sites for Na<sup>+</sup> ion accommodation and higher ionic diffusivity, and then decreased to 372 mAh/g (~93% capacity retention) over 110 cycles. This value was superior to those of previous reports [3,7,18,19] and ~140% higher than the pure Cu<sub>1.8</sub>S-C. The capacity reversibility (Coulombic efficiency) was measured as nearly 100% (see Figure S9). The specific capacity of the Cu<sub>1.8</sub>S-C sample

was higher than the  $\text{Cu}_{1.8}\text{S-C/C}$  up to 78 cycles; however, it kept decreasing from 628 to 266 mAh/g (~42% capacity retention) over the entire cycle process. Furthermore, the  $\text{CuS-C}$  and  $\text{Cu}_2\text{S-C}$  samples showed specific capacities of 155 and 110 mAh/g after 110 cycles and their corresponding capacity retentions of ~16 and ~26%, respectively. The superior capacity retention with higher specific capacity of the  $\text{Cu}_{1.8}\text{S-C/C}$  is attributed to the role of the nanocarbon layer covering the  $\text{Cu}_{1.8}\text{S-C}$  structure. This layer is thought to buffer against the mechanical stress caused by volume variation of the  $\text{Cu}_{1.8}\text{S}$  structure during cycling and to alleviate a structural pulverization of the  $\text{Cu}_{1.8}\text{S}$ , therefore enabling the improved cycling performance. Furthermore, the nanocarbon can enhance the electrical conductivity of the  $\text{Cu}_{1.8}\text{S}$  and tether sodium sulfide ( $\text{Na}_x\text{S}$ ) to prevent its dissolution into electrolytes and the loss of active materials [20]. Figure 8d illustrates the C-rate capability of each sample, the change of specific capacity as a function of the C-rate. Noticeably, the  $\text{Cu}_{1.8}\text{S-C/C}$  sample exhibited average specific capacities of 395, 372, 358, 333, 300, and 286 mAh/g at the rates of 0.1, 0.5, 1, 2, 4, and 5 C, respectively, and high cycling stability; these values were superior to the previous reports [3,18,19]. When the C-rate went back to 1 C, the  $\text{Cu}_{1.8}\text{S-C/C}$  anode returned back to an average capacity of 345 mAh/g, close to the original value at the same C-rate, suggesting the excellent C-rate capability. However, for the pure  $\text{Cu}_{1.8}\text{S-C}$  sample, we found the higher capacities at lower C-rates (0.1, 0.5, and 1 C), but the lower capacities at higher C-rates (2, 4, and 5 C) relative to the  $\text{Cu}_{1.8}\text{S-C/C}$  sample. Furthermore, we observed the capacity decay of the  $\text{Cu}_{1.8}\text{S-C/C}$  sample with the cycle irrespective of C-rates. The better cycling stability of the  $\text{Cu}_{1.8}\text{S-C/C}$  also supports the aforementioned roles of the nanocarbon layers coated on the  $\text{Cu}_{1.8}\text{S-C}$  structure.



**Figure 8.** Electrochemical performance of the  $\text{Cu}_x\text{S-C}$  and  $\text{Cu}_{1.8}\text{S-C/C}$  anode structures. (a) CV curves of the  $\text{Cu}_x\text{S-C}$  and  $\text{Cu}_{1.8}\text{S-C/C}$  anode structures in the voltage range of 0.01–3 V at a scan rate of 0.2 mV/s for the second cycle; (b) characteristic voltage profiles of the  $\text{Cu}_x\text{S-C}$  and  $\text{Cu}_{1.8}\text{S-C/C}$  anode structures; (c) cycling performance of the  $\text{Cu}_x\text{S-C}$  and  $\text{Cu}_{1.8}\text{S-C/C}$  anode structures; (d) comparative study on C-rate capability between the  $\text{Cu}_{1.8}\text{S-C}$  and  $\text{Cu}_{1.8}\text{S-C/C}$  anode structures.

#### 4. Conclusions

We have designed and fabricated a nanoporous  $\text{Cu}_{1.8}\text{S-C/C}$  core/shell anode structure with a high surface area by utilizing MOF-199 as a sacrificial template through a two-step process of sulfurization and carbonization via  $\text{H}_2\text{S}$  gas-assisted PECVD and subsequent hydrothermal-annealing processes. With this anode structure, we achieved a superior SIB performance of  $\sim 93\%$  capacity retention in conjunction with a specific capacity of 372 mAh/g after 110 cycles, compared to the pure  $\text{Cu}_{1.8}\text{S-C}$ . The higher SIB performance emerged from the decisive contribution of the low-degree graphitic carbon layers covered on the  $\text{Cu}_{1.8}\text{S-C}$  to buffer effectively against mechanical stresses induced by volume variation of the  $\text{Cu}_{1.8}\text{S-C}$  during cycling, improve electrical conductivity, and tether the  $\text{Na}_x\text{S}$  to circumvent its dissolution into an electrolyte. The experimental considerations that have hindered this form of battery technology can be resolved with advanced materials. Considering such physico-chemical and electrochemical properties, we confirmed that the  $\text{Cu}_x\text{S-C/C}$  core/shell structure should be implemented with the ever-increasing development of large-scale and advanced SIBs.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/1996-1944/12/8/1324/s1>, Figure S1: A dicopper(II) tetracarboxylate building block for MOF-199 with key distances of Cu–Cu 2.628(2) Å, Cu–OCO 1.952(3) Å and Cu–OH<sub>2</sub> 2.165(8) Å. Figure S2: EDS mapping and spectral analysis for the CuS-C structure sulfurized and carbonized at 350 °C. Notice that the Si and O peaks are associated with the Si/SiO<sub>x</sub> substrate for the EDS analysis. Figure S3: EDS mapping and spectral analysis for the  $\text{Cu}_{1.8}\text{S-C}$  structure sulfurized and carbonized at 550 °C. Figure S4: EDS mapping and spectral analysis for the  $\text{Cu}_2\text{S-C}$  structure sulfurized and carbonized at 650 °C. Figure S5: EDS mapping and spectral analysis for the as-synthesized MOF-199 structure is shown above. The results are summarized in the below graph in which the bound states of Cu exhibit a higher emission spectra (keV). No extraneous peaks were observed suggesting clean synthesis, processing and purification except the Si peak corresponding to the Si/SiO<sub>x</sub> substrate. Figure S6: HRTEM images to demonstrate the core/shell structure of the  $\text{Cu}_{1.8}\text{S-C/C}$  sample showing the interlayer distance ( $\sim 0.27$  nm) of  $\text{Cu}_{1.8}\text{S}$  (200) plane and the thickness ( $\sim 2.6$  nm) of carbon coating layer (C). Figure S7: EDS line scanning results of a  $\text{Cu}_{1.8}\text{S-C/C}$  core-shell structure to identify the distribution of elemental S and C present in the structure. Figure S8: Raman spectra of the  $\text{Cu}_{1.8}\text{S-C}$  structure sulfurized and carbonized at 550 °C. Figure S9: Cycling performance and its corresponding Coulombic efficiency of the  $\text{Cu}_{1.8}\text{S-C/C}$  anode structure at 2 C for 110 cycles.

**Author Contributions:** Conceptualization, C.K., Y.L., and H.-J.L.; methodology, C.K. and Y.L.; formal analysis, T.H.L.; investigation, C.K. and Y.L.; resources, S.H., I.K., J.L., Y.M., S.Y., W.-S.Y., and S.K.; data curation, C.K.; writing, original draft preparation, C.K.; writing, review and editing, Y.L.; supervision, C.K. and H.-J.L.; project administration, C.K. and S.H.; funding acquisition, C.K. and S.H.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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