

Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Layered Ternary Sulfide CuSbS₂ Nanoplates for Flexible Solid-State Supercapacitors

Karthik Ramasamy,^{1} Ram. K. Gupta,² Hunter Sims,³ Soubantika Palchoudhury,⁴ Sergei Ivanov,¹ Arunava Gupta^{4*}*

¹Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Albuquerque, NM-87185¹

²Department of Chemistry, Pittsburg State University, Pittsburg, KS-66762.

³German Research School for Simulation Science, Jülich, Germany-52425

⁴Center for Materials for Information Technology, The University of Alabama, Tuscaloosa, AL-35487

Email: kramasamy@lanl.gov; agupta@mint.ua.edu

Abstract:

Layer-structured materials are advantageous for supercapacitor applications owing to their ability to host a variety of atoms or ions, large ionic conductivity and high surface area. In particular, ternary or higher-order layered materials provide a unique opportunity to develop stable supercapacitor devices with high specific capacitance values by offering additional redox sites combined with the flexibility of tuning the interlayer distance by substitution. CuSbS_2 is a ternary layered sulfide material that is composed of sustainable and less-toxic elements. We report the results of a systematic study of CuSbS_2 nanoplates of varying thickness (4.3 ± 1.4 to 105 ± 5.5 nm) for use as supercapacitors along with the effect of ionic size of electrolyte ions on the specific capacitance and long-term cycling performance behavior. We have obtained specific capacitance values as high as 120 F/g for nanoplates with thickness of 55 ± 6.5 nm using LiOH electrolyte. Electronic structure calculations based on density functional theory predict that with complete surface coverage by electrolyte ions a specific capacitance of over 1160 F/g is achievable using CuSbS_2 , making it a very attractive layer-structured material for supercapacitor applications. Additionally, the calculations indicate that lithium ions can be intercalated between the van der Waals layers without significantly distorting the CuSbS_2 structure, thereby further enhancing the specific capacitance by 85 F/g. Quasi-solid-state flexible supercapacitor devices fabricated using CuSbS_2 nanoplates exhibit an aerial capacitance value of 40 mF/cm^2 with excellent cyclic stability and no loss of specific capacitance at various bending angles. Moreover, the supercapacitors are operable over a wide temperature range. We have further compared the electrochemical behavior of CuSbS_2 with other non-layered phases in the system, namely Cu_3SbS_3 , Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ that clearly highlight the importance of the layered structure for enhancing charge storage.

Keywords: Copper Antimony Sulfide, Layered Sulfide, Nanoplates, Supercapacitors, Electronic Structure

1. Introduction

The novel properties of layer-structured materials at the nano-scale offer exciting opportunities for the development of energy-relevant technologies.^{1,2} In recent years there has been renewed interest in investigating a variety of layered materials triggered in large part by the huge success of graphene.³⁻⁵ With reduced dimensions these materials often exhibit exceptional transport characteristics, mechanical stability and large surface area, which are essential for nano-dimensional electronics, catalysis, sensing and energy storage applications.^{1,6-9} The list of layer-structured materials that have been investigated include oxides, chalcogenides, carbides, nitrides, hydrides, hydroxides, phosphates, and phosphonates.^{10,11,12} Among them, the metal chalcogenides have been the most extensively studied because of their thickness-dependent quantum confinement effects resulting in enhanced optical and electrical properties at reduced thicknesses.^{13,14,15} An area that has thus far not received much attention is the use of layer-structured nanomaterials for supercapacitor applications. The large surface area and van der Waals gap can be exploited for the efficient adsorption and transport of electrolytes, which are desirable for charge storage and discharge processes.^{16,17}

Supercapacitors store and release energy instantaneously, possess long-term stability and are much safer to handle as compared to batteries.¹⁸ These characteristics make them attractive for use in electrical vehicles, consumer electronics, memory back-up systems and other applications where a burst supply of energy is required.^{19,20} Traditional supercapacitors based on carbonaceous materials work through the electrical double-layer capacitance mechanism that limits their energy density.²¹ A significant improvement in energy density can be achieved by use of metal oxide pseudocapacitors.^{22, 23} However, their long-term stability is limited due to the volume change that occurs during charging and discharging processes and also unexpected secondary reactions that lead to degradation of the electrode materials.^{24, 25,26} In contrast, layered materials that are separated by weak van der Waals forces can withstand large volume changes and can also host a variety of foreign atoms or ions between layers.²⁷ Moreover, the graphene-like architecture in these materials is well suited for investigating unique transport properties at reduced dimensions.^{17,28,29} In this regard, a few layer-structured materials have been investigated for supercapacitor applications, including Ti_3C_2 , MoS_2 and SnSe .^{17,27,30} However, the investigations have thus far primarily focused on binary layered materials. Ternary or higher-order layered materials are potentially advantageous for supercapacitor applications over the

binary ones as they offer additional redox sites (i.e., pseudo-capacitance sites) and greater tunability of the inter-layer distance by suitable substitution.³¹ These exceptional characteristics of ternary and higher order layered materials provide a unique opportunity to develop stable supercapacitor devices with high specific capacitance values.

With the aim of developing high stability supercapacitor devices based on ternary or higher-order layered materials, we have investigated copper antimony sulfide (CuSbS_2), which is composed of sustainable and less-toxic elements. CuSbS_2 is a ternary layered sulfide that crystallizes in an orthorhombic crystal system with *Pnma* space group.^{32,33} The crystal structure comprises of SbS_2 and CuS_3 interconnected chains that layer perpendicular to the *c*-axis. In each sheet, cage-like arrangements that are formed by the stacking of six member S-Cu-S-Sb-S-Cu rings in a chair conformation adding to the existing van der Waals intercalation gap for intercalating atoms or ions.^{32,33} Because of its direct band gap at solar wavelengths and high absorption coefficient ($>10^4 \text{ cm}^{-1}$), CuSbS_2 has been studied for solar cell applications.^{34,35,36,37} However, its unique capacity for intercalation have not been investigated for energy storage applications except in our recent preliminary study on mesocrystals of $\text{CuSbSe}_x\text{S}_{1-x}$.³⁸ Herein, we report results of a systematic study of CuSbS_2 nanoplates with varied thicknesses for use in supercapacitors. In addition, we have investigated the effect of ionic size of electrolyte cations on the specific capacitance of CuSbS_2 and its long-term cycling performance behavior. Our results indicate that significant enhancement in the supercapacitance values can be achieved using different thickness nanoplates as compared to previously reported mesocrystals of CuSbS_2 . For better understanding of the electrochemical properties we have determined the open-circuit voltage and specific capacity of CuSbS_2 monolayers using first-principle calculations for different electrolyte cations. Based on the findings we fabricated quasi-solid-state flexible supercapacitor devices using CuSbS_2 nanoplates that exhibit an aerial capacitance value of $\sim 40 \text{ mF/cm}^2$ with excellent cyclic stability and no loss of specific capacitance at various bending angles. Moreover, we have investigated the temperature-dependent electrochemical behavior and charge-discharge characteristics of the CuSbS_2 supercapacitor devices to evaluate their applicability over a wide temperature range. Finally, we have compared the electrochemical behavior of CuSbS_2 nanoplates with nanocrystals of other phases in the Cu-Sb-S system, namely Cu_3SbS_3 , Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ that clearly highlight the importance of the layered structure for enhancing charge storage. The applicability of CuSbS_2 nanoplates both for solar energy

conversion and energy storage applications bring them a step closer towards the fabrication of Single Component Solar Cell-SuperCapacitor (SC)³ devices.

2. Experimental Section

2.1. Chemicals

All chemicals were used as received. Antimony chloride ($\text{SbCl}_3 \cdot 6\text{H}_2\text{O}$, 99.5%) was received from Alfa Aesar; copper acetylacetonate ($\text{Cu}(\text{acac})_2$, $\geq 99.0\%$), and 1-oleylamine (OLA, $\geq 80-90.0\%$) were obtained from Acros Organics and Pfaltz and Bauer, respectively Analytical grade hexane and ethanol were obtained from Aldrich Chemical Co.

2.2. Synthesis of CuSbS_2 nanoplates

For the synthesis of CuSbS_2 nanoplates, $\text{Cu}(\text{acac})_2$ (0.5 mmol), $\text{SbCl}_3 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) and oleylamine (OLA, 10 mL) were degassed and then backfilled with nitrogen. The reaction mixture was heated to targeted reaction temperature. In another vessel, sulfur (1.3 mmol) was dispersed in 1 mL of oleylamine. The sulfur solution was quickly introduced into the metal source mixture held at the synthesis temperature for 10-30 min. The product was isolated by addition of hexane (15 mL) and ethanol (15 mL) followed by centrifugation (4000 rpm/5 min). We also synthesized other Cu-Sb-S phases (Cu_3SbS_3 , Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) in the form of nanocrystals for capacitance studies following procedures reported previously.³⁶

2.3. Measurements

Transmission electron microscopy (TEM) analysis was performed using a FEI-Tecnai, 200 kV transmission electron microscope. Powder XRD patterns were recorded on a Bruker D8 instrument equipped with Cu $K\alpha$ radiation source operated as a rotating anode at 40 kV and 20 mA. Scanning electron microscope (SEM) analysis was carried out using a JEOL 7000 FE SEM equipped with energy dispersive X-ray spectroscopy (EDX). The X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Kratos Axis Ultra spectrometer employing a monochromated Al $K\alpha$ X-ray source with analyzer pass energy of 80 eV for survey scans and 20 eV for elemental scans. Spectra were analysed by first subtracting a Shirley background and then obtaining accurate peak positions by fitting peaks using a mixed Gaussian/Lorentzian line shape. All photoelectron binding energies (BE) are referenced to C 1s adventitious peak set at 285 eV BE. The analyser was calibrated using elemental references; Au $4f_{7/2}$ (83.98 eV BE), Ag $3d_{5/2}$ (368.26 eV BE) and Cu $2p_{3/2}$ (932.67 eV BE).

2.4. Methods (Theory)

Calculations were performed using the Vienna *ab-initio* Simulation Package (VASP)^{39,40,41} within the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) to density functional theory.^{42,43} We used the projected augmented-wave (PAW) pseudopotentials of Kresse and Joubert.^{44,45} and a plane wave cut off energy of 550 eV. The surface calculations were converged with respect to vacuum width (about 10 Å) and k-points (a 12x12x1 Monkhorst-Pack grid for a single unit cell), and all forces were minimized to within 0.05 eV/Å. Positions of adatoms were optimized with the rest of the CuSbS₂ surface remaining fixed. The open-circuit voltage was calculated on a 3x3x1 supercell to reduce inter-adatom interaction and compute the energy of formation of the surface with adsorbate via

$$\Delta E_f = \frac{1}{N} [E_{sub+ad} - (E_{sub} + nE_{ad})] \quad (1)$$

where N is the number of formula units of CuSbS₂ and n is the number of adsorbed ions in the full system. E_{ad} is the energy of a single BCC Li, Na, or K primitive cell. The open-circuit voltage is then given by $-\Delta E_f/x$, where x is the number of ions per formula unit.

2.5. Electrochemical measurements

Electrochemical measurements were carried out using platinum wire and saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The working electrode was obtained by mixing of CuSbS₂ nanoplates (80 wt.%), acetylene black (10 wt.%) and polyvinylidene difluoride (PVDF, 10 wt.%) in N-methyl-2-pyrrolidinone (NMP) and pasting onto a nickel foam, followed by drying at 60 °C under vacuum. KOH, NaOH and LiOH (3M) were used as electrolytes. The charge storage capacity of the materials was tested using cyclic voltammetry (CV) and galvanostatic charge-discharge methods.⁴⁶ The specific capacitance (C_{sp}) values from charge-discharge measurements were calculated using the following expression.⁴⁷

$$C_{sp} = \frac{I \times \Delta t}{\Delta V \times m} \quad (2)$$

where I is the discharge current (A), Δt is the discharge time (s), ΔV is the potential window, and m is the mass (g) of the active material. Electrochemical measurements were performed on a VersaSTAT 4-500 electrochemical workstation (Princeton Applied Research, USA). Quasi solid-

state device was fabricated by sandwiching two electrodes separated by ion transporting layers. Potassium hydroxide and lithium hydroxide were used as electrolytes.

3. Results and Discussions

Nanoplates of CuSbS_2 have been synthesized following our earlier reported procedure.³¹ In brief, 1 mL of sulfur in oleylamine was introduced into the reaction mixture of $\text{Cu}(\text{acac})_2$ and SbCl_3 in oleylamine at 170 °C. The reaction produced nanoplates with thickness of 4.3 ± 1.4 nm and edge dimensions of about 450 nm for 10 min reaction time. Reactions at higher reaction temperatures and longer reaction times produce thicker plates, with the lateral dimensions being closely maintained. The CuSbS_2 structure consists of quadruple layers bound together by van der Waals forces (Figure 1a). The Sb in one layer and S in the adjacent layer of the structure are separated by a distance of ~ 3.115 Å, which is larger than the interlayer gap distance (2.051 Å). An expanded portion of one of the layers is shown in Figure 1(b). A cage-like arrangement formed by stacking of six member (S-Cu-S-Sb-S-Cu) rings in chair conformation is apparent from the structure. The distances between two atoms of the same type in the cages are between 5.3 Å and 6.19 Å.³² Powder X-ray diffraction (XRD) was used for the determination of phase purity. Diffraction peaks corresponding to the orthorhombic structure of CuSbS_2 are observed, with no trace of the binary sulfides of copper or antimony. XRD patterns in Figure 1(c) obtained from CuSbS_2 nanoplates synthesized at different temperatures are in good agreement with orthorhombic CuSbS_2 phase (ICDD: 044-1417). Furthermore, the FWHM value of each peak decreases with increasing growth temperature, indicating increase in the crystallite size. In order to characterize the chemical constituents on the surface, we have carried out x-ray photoelectron spectroscopy (XPS) measurements on the CuSbS_2 nanoplates. The qualitative XPS survey spectrum for CuSbS_2 nanoplates is provided in Figure S1(a). The surface survey spectrum exhibits peaks corresponding to Auger electron ejection for Cu, Sb and S, along with C and O. No peaks from any other impurities were observed. High resolution XPS spectra in Figure S1 (b) - (d) of Cu 2*p*, Sb 2*p*, S 2*p* from CuSbS_2 nanoplates confirm the expected oxidation state of each element. The binding energy peaks at 930.3 eV and 950.2 eV, with an energy difference of 19.9 eV, can be assigned to 2*p*_{3/2} and 2*p*_{1/2} of Cu (I). For Sb (II), the doublet peaks at 528.3 eV (3*d*_{5/2}) and 537.4 eV (3*d*_{3/2}) with an energy separation of 9.1 eV are observed. High resolution XPS peaks for sulfur as a sulfide appear at 161.4 eV (2*p*_{3/2}) and 162.6 eV (2*p*_{1/2}) with a small energy difference of 1.2 eV.⁴⁸ We have additionally estimated the elemental composition of the

nanoplates using scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX). The analysis results provide a composition ratio of 1:1:1.95 (Cu: Sb: S) for the nanoplates with a slight deficiency in sulfur content.

Transmission electron microscope (TEM) was used in the identification of nanocrystals morphology and size. Plate-like morphology was observed from TEM images in Figure 2(a)-(d). The edge-edge length of the nanoplates varied from 400 ± 25 nm to 450 ± 20 nm for the growth time between 10 and 30 min at 170 °C with thickness from 4.3 ± 1.4 nm and 10.0 ± 0.7 nm (Figure 2 (e) - (l)). At higher temperatures (190-280 °C) the sizes were found to be between 300 ± 20 nm and 335 ± 25 nm and thickness of 19 ± 1 nm to 105 ± 5.5 nm. Average lattice distance (0.302 ± 0.003 nm) of the surface of nanoplates obtained from HRTEM image in Figure S2 (a) are in very well agreement with the (200) planes of orthorhombic CuSbS₂.

The electrochemical properties of nanoplates with different thickness were investigated by cyclic voltammetry and galvanostatic charge-discharge methods. Figure 3(a) shows the cyclic voltammetry (CV) curves of different thickness CuSbS₂ nanoplates at a scan rate of 50 mV/s using KOH as the electrolyte. A pair of reversible redox waves indicating the pseudocapacitance feature at essentially the same potential values is apparent from the CV curves of different thickness CuSbS₂ nanoplates (Figure 3(a)). With increasing scan rate, the CV curves maintain their shapes but exhibit increased peak currents (Figure S3). A concurrent increase in the ΔE_{wave} (difference between E_p^a and E_p^c) value is observed with a linear relationship for the wave current as a function of the square root of scan rate (Figure S4), indicating diffusion-controlled reaction kinetics during the redox process. From the CV curves in Figure 3(a) a systematic increase in the current density can be noted with increasing nanoplate thickness followed by a decrease for the largest thickness, with the 55 ± 6.5 nm thick nanoplates displaying the highest current density. The thinner nanoplates are expected to exhibit higher current density due to the larger available surface area for redox reactions, but here we observe a reverse trend. From the analysis of the SEM and TEM images (Figures S5 and 2, respectively) it appears that the thin plates readily aggregate, which leads to reduction of their surface area and, as such, to the reduction of the current density. As the thickness of plates increase, their agglomeration diminishes, leading to the temporary increase in the surface area. However, further increase in particle thickness will again lead to the decrease in the surface area and the decrease in the

current density. The current density trend with increasing thickness of the nanoplates trend is also reflected in the specific capacitance values deduced from CV curves at various scan rates.

We have additionally studied the charge storage capacity of CuSbS_2 electrodes using galvanostatic charge-discharge measurements at various applied current. The representative discharge characteristics of CuSbS_2 nanoplate (7.2 ± 1.4 nm) electrode is shown in Figure 3(b) as a function of discharge current. As seen, the discharge time decreases with increasing discharge current. The variation of specific capacitance with discharge current for nanoplates of different thicknesses is shown in Figure 3(c). The C_{sp} values for 55 ± 6.5 nm thick nanoplates with KOH as electrolyte are determined to be 100, 96, 94, 92, 89, 92, 99 F/g at applied currents of 0.4, 0.6, 0.8, 1, 2, 3, 4 mA, respectively. The energy density and power density values (Ragone plot) calculated using the respective specific capacitance values is given in Figure 3(d). These values are higher than those for CuSbE_2 ($E = \text{S}$ or Se) mesocrystals and comparable to the specific capacitance values reported for other chalcogenide nanocrystals (SnSe , CoS , CuS).^{49,30,50,38} The observed decrease in specific capacitance with increasing discharge current in some cases is likely due to higher potential drop and incomplete Faradic redox reaction of the active materials at higher discharge currents.

We investigated the long term cyclic stability of CuSbS_2 nanoplate electrodes by carrying out CV measurements up to 1000 cycles. The representative CV curves of 7.2 ± 1.4 nm thick nanoplates are shown in Figure 3(e). The wave profile and the area of the voltammograms appear to remain essentially unchanged, indicating the high cyclic voltammetric stability of the nanoplates without any significant volume change. Furthermore, the absence of additional redox waves in the CV curves confirms the absence of any new redox species in the process of CV cycling. However, a systematic increase in the reduction potential can be seen with increasing number of CV cycles suggesting increased intercalation of electrolyte ions between the layers.

Layer-structured materials are known to host atoms or ions that are smaller than the interlayer gap. CuSbS_2 is a ternary layered sulfide material having an interlayer gap of 2.051 \AA , sufficiently wide to host atoms or ions between the layers. Depending on the size of intercalates in the electrolytes, the specific capacitance of the material can be varied. With this perspective, we have carried out cyclic voltammetry measurements using LiOH , NaOH and KOH electrolytes. Figure 4(a) shows CV measurements on CuSbS_2 electrode using these three electrolytes. It can be noticed from the CV curves that the electrolyte with the smallest cationic

radii (LiOH) has the highest reduction potential value. Indeed, the reduction potential exhibits an inverse relationship with the size of the electrolyte cation. Being the smallest ion, it is likely that Li^+ most effectively intercalates between the layers and inside of the crown-like cages of CuSbS_2 . Because of the deeper intercalation, higher potential is required for Li^+ reduction. The specific capacitance values determined from the charge-discharge characteristics of CuSbS_2 nanoplates (55 ± 6.5 nm) at various applied currents using the three different electrolytes are provided in Figure 4(b). The trend in specific capacitance values parallel the CV results, with LiOH showing the highest specific capacitance. We obtained specific capacitance values of 115-120 F/g at applied current values from 0.6-5 mA, with noticeably higher specific capacitance than those obtained for NaOH and KOH (Ragone plot of power density versus energy density is given in Figure 4(c)). Furthermore, we have tested the cyclic stability of CuSbS_2 nanoplates in these electrolytes using galvanostatic charge-discharge characteristics. Figure 4(d) shows the cyclic stability of CuSbS_2 electrode consisting of 55 ± 6.5 nm thick nanoplates using LiOH as electrolyte. A gradual increase in specific capacitance followed by the retention of essentially 100% of its value is observed even after 1000 cycles of charge-discharge measurements in LiOH. However, in the case of KOH an amplification of specific capacitance is recorded with increase of specific capacitance nearly by 47% on continuing the charge-discharge up to 5000 cycles (Figure 4(e) and 5(a)). This is noteworthy since most other oxide and chalcogenide-containing supercapacitor materials severely lack long-term cyclic stability. The observed increase in specific capacitance using KOH electrolyte is likely caused by gradual intercalation of K^+ ions between the layers or possible intercalation and exfoliation of the layers. This phenomenon relating to intercalation of electrolyte ion has been reported for the similar layered structure materials MoS_2 supercapacitor using NaOH as electrolyte.¹⁷ Figure 5(b) shows the Ragone-plot of the specific capacitance with number of cycles. The plot shows an initial gradual increase in the energy density with power density up to about 1100 cycles followed by a sharp energy density increase from 2.6 Wh/kg (1100th cycle) to 3.8 Wh/kg (5000 cycles). The observed increase in energy density with increasing number of cycles further supports the proposed model of intercalation of electrolyte ions between the layers of CuSbS_2 . The inset to Figure 4(d) shows the last few charge-discharge cycles for the CuSbS_2 (55 ± 6.5 nm) nanoplates electrode.

To better understand the interaction of different electrolyte ions with CuSbS_2 , we have determined the open-circuit voltage (OCV) and specific capacity of CuSbS_2 monolayers within

density functional theory framework. Optimization of the adatom positions (Li^+ , Na^+ or K^+) indicates the preferred location of the ions over the copper sites rather than the S or Sb sites. In Figure 6(a), we have plotted the valence charge densities (relative to the unbonded densities) for all three $3 \times 3 \times 1$ systems. All three indicate charge transfer from the adsorbed ion to the surface. The partial densities of states for the adatoms (Figure 6(b)) lend support to the picture suggested by the charge densities: the valence s electron is almost completely transferred to the host system.

We compute the OCV over a Cu site for Li, Na, and K ions adsorbed onto the CuSbS_2 surface to be 0.390 eV, 0.461 eV, and 0.812 eV, respectively. These values follow the expected trend for adsorbed ions of increasing size but do not agree with Figure 5a. Instead, the measured behavior may indicate that intercalation rather than adsorption is dominant, as larger ions could be more difficult to accommodate between layers. This is evident in our relaxed intercalated structures: Na and K ions seem to displace the nearest Sb ion, driving it into the "bulk" of the layer (see Supporting Information Figure S6). We find that Li, Na, and K have intercalation voltages (compared to the undisrupted host system) of 0.228 eV, 0.909 eV, and 0.581 eV. This non-monotonicity reflects the greater energy cost of distorting the CuSbS_2 system to allow the intercalated K ions, but we still do not recover the observed behavior. It is possible that the fully relaxed intercalated structures cannot be achieved in the real many-layer nanoplates. Our calculations do show that the intercalation energies can scale inversely with ionic radius, and partial relaxation would enhance this trend.

The theoretical specific capacity can be estimated via⁵¹

$$C_M = \frac{1}{M_{CAS}} (z x_{max} F)$$

where M_{CAS} is the molar mass of the host CuSbS_2 system, z is the ionic charge (+1), x_{max} is the estimated maximum adatom content (per formula unit), and F is Faraday's constant. To determine x_{max} , we compute the OCV as a function of x on a $2 \times 2 \times 1$ CuSbS_2 surface (Figure 6(c)). We assume that the two surfaces are uncoupled and thus that the true x_{max} is simply twice that of single-sided adsorption. Unlike the simpler transition metal dichalcogenides (TMDCs), the surface of CuSbS_2 is uneven, and ions adsorbed over different ionic sites (Cu, Sb, or S) tend to sit at different heights above the surface. The first adsorbed layer will fully cover the Cu sites

(corresponding to $x = 0.5$), while subsequent adatoms will form additional layers covering the Sb and S sites. Full monolayer coverage (only Cu sites) would give a specific capacity of about 387 F/g for the three ionic adsorbates. For Li and Na, we obtain x_{max} of about 0.8 and 0.9, giving 619 F/g and 697 F/g, respectively. Surprisingly, we find that K retains a positive OCV through $x = 1.5$ (complete coverage of a single surface), which is the highest x we calculated. This would give a specific capacitance of more than 1160 F/g. Our intercalation calculations (without adatoms) show $x_{max} > 0.22$ for Li intercalation (about 85 F/g). This is in reasonable agreement with the measured C_{sp} and it is consistent with the conclusion that the ion intercalation is a dominant process in the real system.

With the aim of developing flexible, quasi-solid-state supercapacitors composed of cost effective and less-toxic materials, we have fabricated supercapacitor devices using LiOH/KOH electrolyte separating two CuSbS₂ electrodes coated on Ni foam. A schematic representation of the device is shown in Figure 7(a). The CV curves of the device at different scan rates are nearly symmetrical and rectangular without presence of any redox peaks (Figure 7(b)). The CV curve characteristics are comparable to devices reported using other materials.¹⁶ The areal capacitance of the device deduced from CV curves at different scan rates is estimated to be 40 mF/cm² at 25 mV/s, which is significantly higher than that for supercapacitor devices fabricated using SnSe and SnSe₂ nanoplates and comparable to MoS₂-based device.^{17,30} Figure 7(c) shows cyclic voltammetry measurements of the quasi-solid-state device up to 4000 cycles at constant scan rate. The excellent electrochemical stability of the device is verified by the absence of redox waves and no visible changes in CV curve shapes and redox currents even after the 4000th cycle when compared with the initial curve. Further to this, galvanostatic charge discharge measurements on the device have been carried out up to 2500 cycles at a constant current in order to investigate its cycling performance (Figure 7(d)). The cyclic performance of a supercapacitor device can be described by two main processes, namely the activation and steady state. The activation period in our device lasts nearly up to 400 cycles with close to 50% increase in the specific capacitance value, as also observed for the CuSbS₂ electrodes. In general, this activation period is significantly longer than, is commonly observed. The prolonged activation period further supports the notion of intercalation of electrolyte ions between the layers and within the cages of CuSbS₂ electrodes. Interestingly, the specific capacitance value is unchanged even after 2500 cycles confirming the device's exceptional stability. In addition, the flexibility of

the device has been investigated by measuring the CV curves at various bending angles. As shown in Figure 7(e), the CV curves do not show any noticeable changes at bending angles of 15, 30 and 45° as compared with the CV curve without any bending. These results clearly demonstrate the potential applicability of CuSbS₂ as a flexible, stable charge storage and delivery system (bending studies of electrode is given in Figure S7).

It is important to develop supercapacitors that can be used under a wide range of environmental conditions. Temperature is clearly one of the major factors that affect device performance. Considering this, we have investigated the electrochemical behavior of our supercapacitor devices at different temperatures. Figure S8 (a) shows CV curves of a *quasi*-solid-state flexible device measured at different temperatures. A systematic increase in the redox current with increasing temperature is apparent from the CV curves, which is reflected in the areal specific capacitance values estimated from CV curves. The highest specific capacitance value is obtained at 55°C, which is nearly 80% higher than the value at room temperature (Figure S8 (b)). The specific capacitance obtained below room temperature (15°C) is somewhat lower (by ~8%) than that at ambient conditions. Despite temperature-dependent changes in specific capacitance values, the CV curves show nearly identical symmetrical shape without appearance of any redox waves at any temperature indicating thermal electrochemical stability of the device. Similar temperature-dependent changes in specific capacitance have also been observed in galvanostatic charge-discharge characteristics of the CuSbS₂ supercapacitor device at different temperatures (Figures S8(c) and (d)).

Extending our investigations of Cu-Sb-S for supercapacitor applications, we have carried out cyclic voltammetry and galvanostatic charge-discharge measurements on nanocrystals of Cu₃SbS₃ (Skinnerite), Cu₃SbS₄ (Fematinite) and Cu₁₂Sb₄S₁₃ (Tetrahedrite) phases. These phases crystallize in non-layered structures: Cu₃SbS₃ in monoclinic, Cu₃SbS₄ in tetragonal and Cu₁₂Sb₄S₁₃ in cubic form. Comparing the electrochemical behavior of these compounds with CuSbS₂ nanoplates, it is possible to appreciate the importance of the layered structure for charge storage applications. We have recently reported the phase-pure synthesis of all four phases of Cu-Sb-S nanocrystals.³⁶ Following these methods, we have synthesized spherical shape Cu₃SbS₃, oblate Cu₃SbS₄ and hollow structure Cu₁₂Sb₄S₁₃ nanocrystals. Representative TEM images of these nanocrystals along with their crystal structures are given in Figure 8(a)-(d). The specific capacitance values determined from charge-discharge characteristics (in KOH) using these

nanocrystals as electrodes and corresponding Ragone plot are shown in the Figure 8(e) and (f). From the figures it is apparent that all these nanocrystals exhibit low specific capacitance in comparison with CuSbS_2 nanoplates, despite having similar compositions and sizes. This clearly illustrates that the layered structure is responsible for efficient insertion and extraction of electrolyte ions during the electrochemical process. Nevertheless, all the non-layered Cu-Sb-S compounds show very good cyclic stability (Figure 9). We also studied the effect of electrolyte ions size on specific capacitance of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ using KOH and LiOH electrolytes and did not observe any appreciable difference in their electrochemical behavior, supporting our conclusion of intercalation of electrolyte ions between the layers in the layer-structured CuSbS_2 nanoplates.

4. Conclusion:

We have systematically studied the effect of thickness on the electrochemical behavior and specific capacitance of CuSbS_2 nanoplates. Electrochemical measurements reveal that nanoplates with thickness of 55 ± 6.5 nm are optimum for obtaining the highest specific capacitance. In addition, we have studied the specific capacitance of CuSbS_2 nanoplates and their long-term cycling performance behavior using different electrolytes, namely LiOH, NaOH and KOH, and found that LiOH provides specific capacitance values as high as 120 F/g. Further, to understand the interaction of different electrolytes with CuSbS_2 , we computed the electronic structure calculations using the density functional theory. Our calculations predict that the electrolyte cations prefer Cu-sites, and with only the Cu-sites occupation, theoretical specific capacitance of 385 F/g can be obtained with all three electrolytes. Interestingly, with complete coverage of CuSbS_2 surface we obtain specific capacitance of 619, 697, and more than 1160 F/g for Li, Na and K respectively. These values are significantly higher than for any layer structured material investigated thus far. In addition, we have found that lithium ions can be intercalated between the van der Waals layers without distorting the CuSbS_2 structure. With lithium ion intercalation, the specific capacitance can further be enhanced by 85 F/g. These investigations strengthen our hypothesis that multiple site adsorption and intercalation can be collectively realized in the ternary layered materials. Our preliminary effort on fabricating quasi-solid-state flexible supercapacitor device using CuSbS_2 nanoplates have provided an aerial capacitance value of 40 mF/cm^2 with excellent cyclic stability and no loss of specific capacitance at various bending angles, with operability over a wide temperature range. Our comparative study of CuSbS_2 nanoplates with non-layer structure phases in the Cu-Sb-S system Cu_3SbS_3 , Cu_3SbS_4 and

$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ clearly highlight the importance of the layered structure for enhancing charge storage. The remarkable theoretical capacitance with excellent cyclic stability in corrosive electrolytes and direct gap visible light absorption with large absorption coefficient properties of ternary layer sulfide CuSbS_2 , motivates the construction of Single Component Solar Cell-SuperCapacitor (SC)³ devices These are currently under investigation and the results will be reported elsewhere.

Supporting Information.

XPS data, HRTEM images, SEM images, CV curves.

Notes

The authors declare no competing financial interest

Acknowledgement

Synthesis, X-ray, TEM and SEM characterization work was done at the University of Alabama, supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-08ER46537. Some of the analysis was also performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Los Alamos National Laboratory, an affirmative action equal opportunity employer, is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. Electrochemical measurements were carried out at Pittsburg State University. Dr. Ram Gupta expresses his sincere acknowledgment to the Polymer Chemistry Initiative, Pittsburg State University for providing financial and research support. Dr. Ram Gupta thanks National Science Foundation Award No. EPS-0903806 and matching support from the State of Kansas through the Kansas Board of Regents

References:

- 1 Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman and M. S. Strano, *Nat. Nanotechnol.*, 2012, **7**, 699–712.

- 2 S. Bertolazzi, D. Krasnozhon and A. Kis, *ACS Nano*, 2013, **7**, 3246–52.
- 3 S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutie, T. F. Heinz, S. S. Hong, J. Huang, A. F. Ismach, E. Johnston-halperin, M. Kuno, V. V Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, O. M. G. Spencer, M. Terrones, W. Windl and J. E. Goldberger, *ACS Nano*, 2013, **7**, 2898–2926.
- 4 K. J. Koski and Y. Cui, *ACS Nano*, 2013, 3739–3743.
- 5 R. R. Nair, H. A. Wu, P. N. Jayaram, I. V Grigorieva and A. K. Geim, *Science*, 2012, **335**, 442–444.
- 6 G. A. Tritsarlis, B. D. Malone and E. Kaxiras, *J. Appl. Phys.*, 2013, **103**, 233507.
- 7 A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli and F. Wang, *Nano Lett.*, 2010, **10**, 1271–5.
- 8 J. Seo, J. Jang, S. Park, C. Kim, B. Park and J. Cheon, *Adv. Mater.*, 2008, **20**, 4269–4273.
- 9 K. S. Novoselov, A. K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, I. V Grigorieva and A. A. Firsov, *Science* ., 2004, **306**, 666–9.
- 10 M. Xu, T. Liang, M. Shi and H. Chen, *Chem. Rev.*, 2013, **113**, 3766–98.
- 11 C. Ataca, H. Sahin and S. Ciraci, *J. Phys. Chem. C*, 2012, **116**, 8983.
- 12 P. Miró, M. Audiffred and T. Heine, *Chem. Soc. Rev.*, 2014, **43**, 6537–54.
- 13 G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen and M. Chhowalla, *Nano Lett.*, 2011, **11**, 5111–6.
- 14 R. Jacobs-Gedrim and M. Shanmugam, *ACS Nano*, 2014, **8**, 514–521.
- 15 S. Lei, L. Ge, S. Najmaei, A. George, R. Kappera, J. Lou, M. Chhowalla, H. Yamaguchi, G. Gupta, R. Vajtai, A. D. Mohite and P. M. Ajayan, *ACS Nano*, 2014, **8**, 1263–1272.
- 16 S. Ratha and C. S. Rout, *ACS Appl. Mater. Interfaces*, 2013, **5**, 11427.
- 17 L. Cao, S. Yang, W. Gao, Z. Liu, Y. Gong, L. Ma, G. Shi, S. Lei, Y. Zhang, S. Zhang, R. Vajtai and P. M. Ajayan, *Small*, 2013, **9**, 2905.
- 18 P. Simon and Y. Gogotsi, *Nat. Mater.*, 2008, **7**, 845.
- 19 Y. Zhai, *Adv. Mater*, 2011, **22**, 4828–4850.
- 20 B. Dunn, H. Kamath and J. M. Tarascon, *Science* , 2011, **334**, 928.

- 21 L. Zhang and X. S. Zhao, *Chem. Soc. Rev.*, 2009, **38**, 2520.
- 22 V. Augustyn, P. Simon and B. Dunn, *Energy Environ. Sci.*, 2014, **7**, 1597.
- 23 W. Yan, J. Y. Kim, W. Xing, K. C. Donavan, T. Ayvazian and R. M. Penner, *Chem. Mater.*, 2012, **24**, 2382–2390.
- 24 M. Okubo, E. Hosono, J. Kim, M. Enomoto, N. Kojima, T. Kudo, H. Zhou and I. Honma, *J. Am. Chem. Soc.*, 2007, **129**, 7444–52.
- 25 R. Wang and X. Yan, *Sci. Rep.*, 2014, **4**, 3712.
- 26 E. Mitchell, A. Jimenez, R. K. Gupta, B. K. Gupta, K. Ramasamy, M. Shahabuddin and S. R. Mishra, *New J. Chem.*, 2015.
- 27 M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall’Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum and Y. Gogotsi, *Science*, 2013, **341**, 1502.
- 28 K.-J. Huang, L. Wang, Y.-J. Liu, Y.-M. Liu, H.-B. Wang, T. Gan and L.-L. Wang, *Int. J. Hydrogen Energy*, 2013, **38**, 14027–14034.
- 29 H. S. S. R. Matte, a Gomathi, A. K. Manna, D. J. Late, R. Datta, S. K. Pati and C. N. R. Rao, *Angew. Chem. Int. Ed. Engl.*, 2010, **49**, 4059–62.
- 30 C. Zhang, H. Yin, H. Min, Z. Dai, H. Pang, Y. Zheng, Y.-Q. Lan, J. Bao and J. Zhu, *ACS Nano*, 2014, 3761–3770.
- 31 K. Ramasamy, H. Sims, W. H. Butler and A. Gupta, *J. Am. Chem. Soc.*, 2014, **136**, 1587–1598.
- 32 A. Kyono and M. Kimata, *Am. Mineral.*, 2005, **90**, 162–165.
- 33 M. F. Razmara, C. N. B. Henderson, R. A. D. Pattrick, A. M. T. Bell and J. M. Charnock, *Mineral. Mag.*, 1997, **61**, 79–88.
- 34 J. T. R. Dufton, A. Walsh, P. M. Panchmatia, L. M. Peter, D. Colombara and M. S. Islam, *Phys. Chem. Chem. Phys.*, 2012, **14**, 7229–33.
- 35 B. Yang, L. Wang, J. Han, Y. Zhou, H. Song, S. Chen, J. Zhong, L. Lv, D. Niu and J. Tang, *Chem. Mater.*, 2014, **26**, 3135–3143.
- 36 K. Ramasamy, H. Sims, W. H. Butler and A. Gupta, *Chem. Mater.*, 2014, **26**, 2891–2899.
- 37 K. Ramasamy, B. Tien, P. S. Archana and A. Gupta, *Mater. Lett.*, 2014, **124**, 227–230.

- 38 K. Ramasamy, R. K. Gupta, S. Palchoudhury, S. Ivanov and A. Gupta, *Chem. Mater.*, 2014, 10.1021/cm5041166.
- 39 G. Kresse and J. Hafner, *Physcial Rev. B*, 1993, **47**, 558.
- 40 G. Kresse and J. Hafner, *Physcial Rev. B*, 1994, **49**, 14251.
- 41 G. Kresse and J. Furthmuller, *Comput. Mater. Sci.*, 1996, **6**, 15.
- 42 W. Kohn and L. J. Sham, *physcial Rev.*, 1965, **A140**, 1133.
- 43 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 44 P. E. Blochl, *Physcial Rev. B*, 1994, **50**, 17953.
- 45 G. Kresse and D. Joubert, *Physcial Rev. B*, 1999, **59**, 1758.
- 46 E. Mitchell, R. K. Gupta, K. Mensah-Darkwa, D. Kumar, K. Ramasamy, B. K. Gupta and P. Kahol, *New J. Chem.*, 2014, **38**, 4344.
- 47 J. Gomez and E. E. Kalu, *J. Power Sources*, 2013, **230**, 218–224.
- 48 R. E. Ornelas-Acosta, D. Avellaneda, S. Shaji, G. a. Castillo, T. K. Das Roy and B. Krishnan, *J. Mater. Sci. Mater. Electron.*, 2014, **25**, 4356–4362.
- 49 B. Wang, J. Park, D. Su, C. Wang, H. Ahn and G. Wang, *J. Mater. Chem.*, 2012, **22**, 15750.
- 50 Z. Stevic and M. R. Vujasinovic, *J. Power Sources*, 2006, **160**, 1511.
- 51 D. Er, J. Li, M. Naguib, Y. Gogotsi and V. B. Shenoy, *ACS Appl. Mater. Interfaces*, 2014, **6**, 11173–11179.

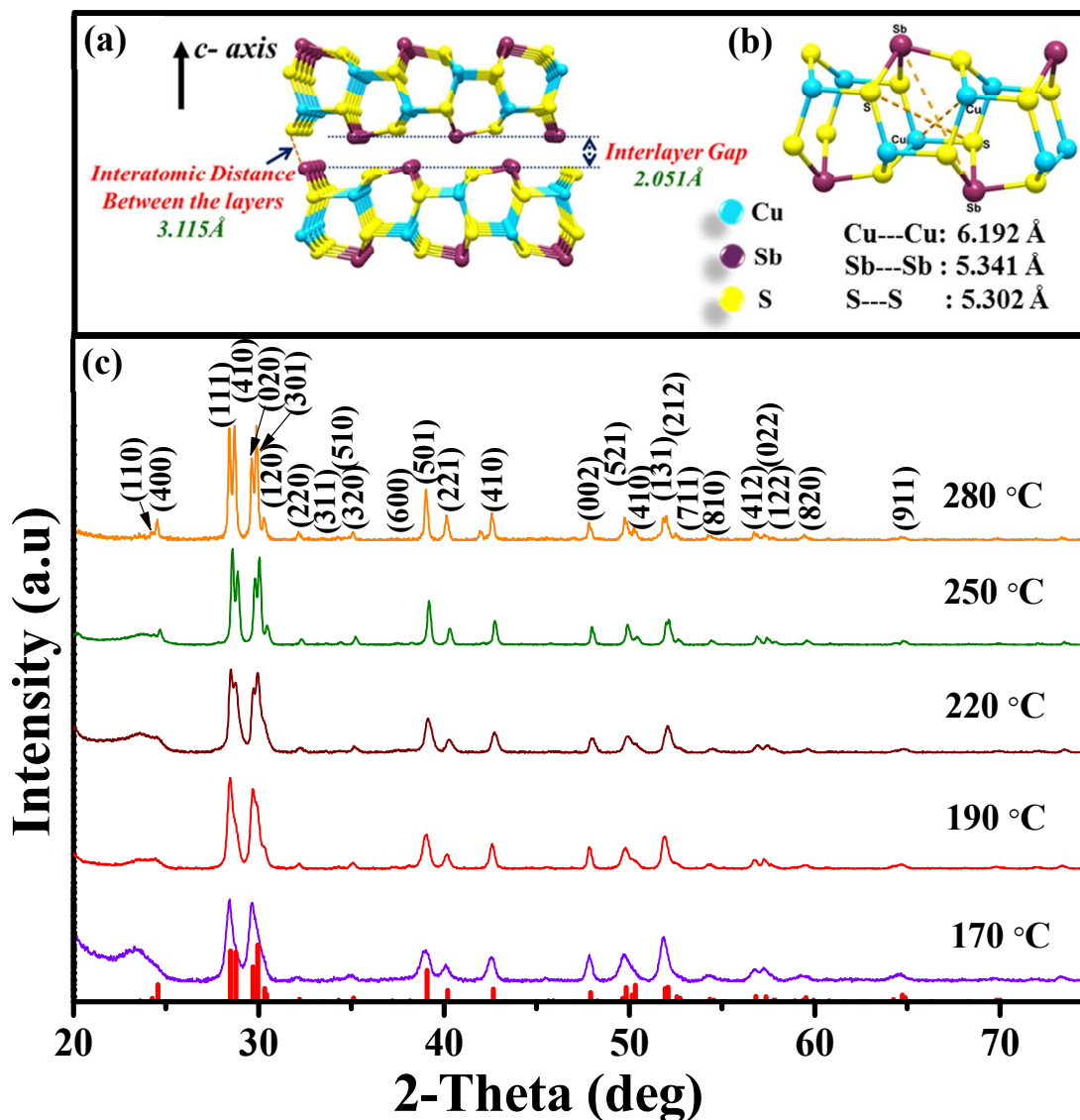


Figure 1. Crystal structures of CuSbS_2 showing (a) the interlayer (van der Waals) gap and distance between two quadruple layers, and (b) cages within a single layer, (c) Powder x-ray diffraction patterns of CuSbS_2 nanoplates synthesized at different temperatures. The standard ICDD pattern (red lines; ICDD: 044-1417) of orthorhombic CuSbS_2 is provided at the bottom.

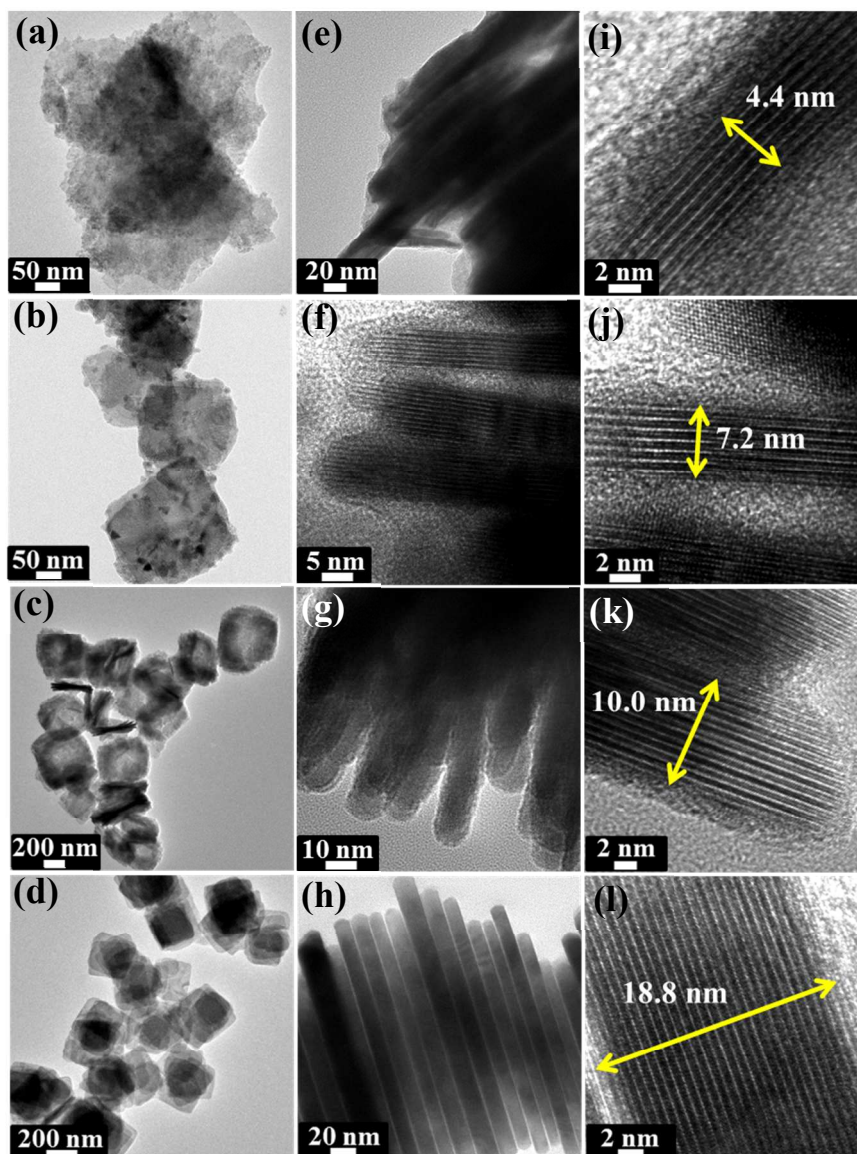


Figure 2. (a)-(d) Top view and (e)-(h) side view TEM images. (i)-(l) Side view HRTEM images of different thickness CuSbS_2 nanoplates.

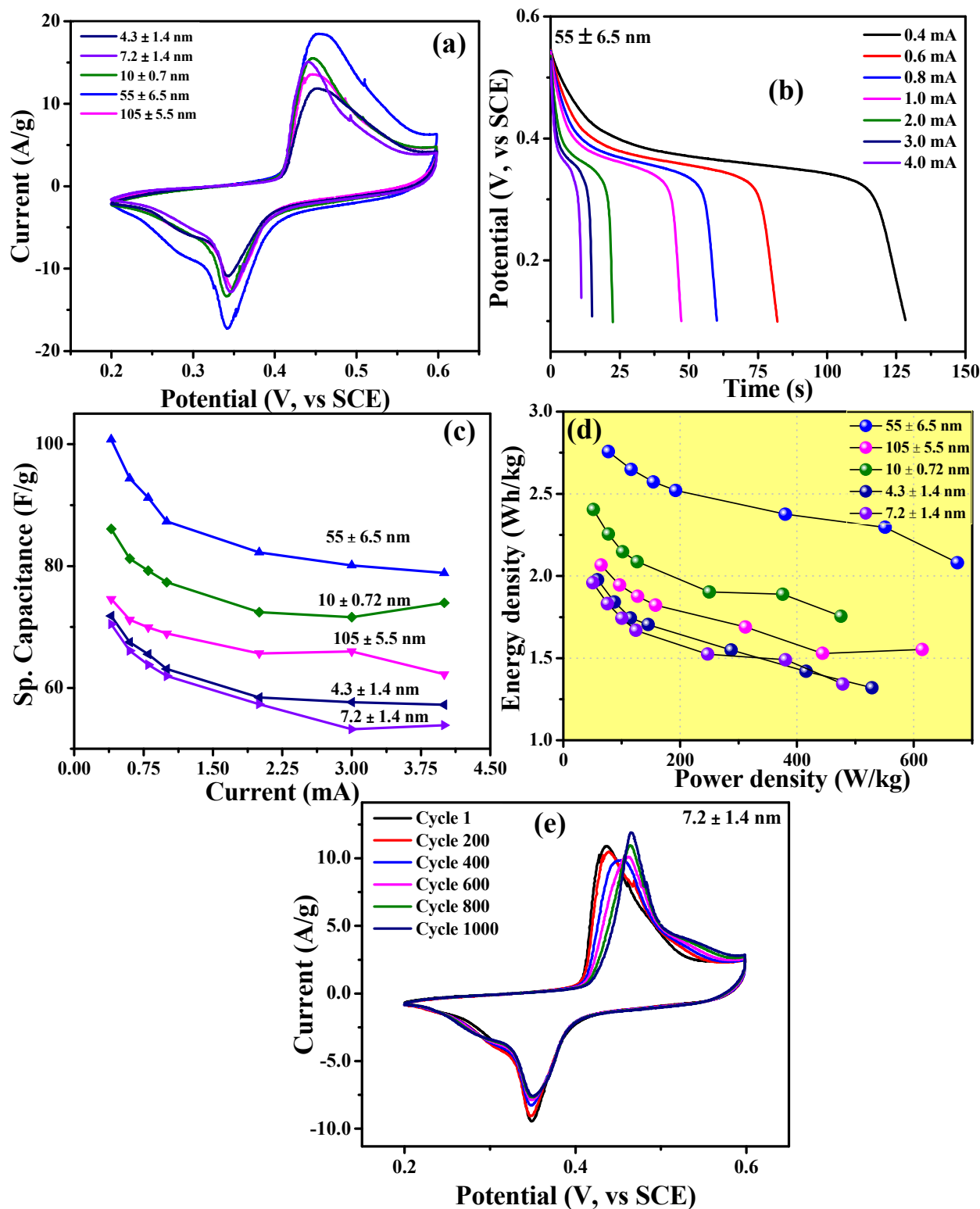


Figure 3. Cyclic voltammogram curves of (a) different thickness CuSbS₂ nanoplates. (b) Galvanostatic charge-discharge characteristics of 55 ± 6.5 nm thick CuSbS₂ nanoplates at different applied current. (c) Variation in specific capacitance of different thickness CuSbS₂ nanoplates with applied current. (d) Ragone plot for different thickness nanoplates. (e) Cyclic voltammogram curves showing cyclic stability of 7.2 ± 1.4 nm CuSbS₂ nanoplates. All the data were obtained with using KOH as electrolyte.

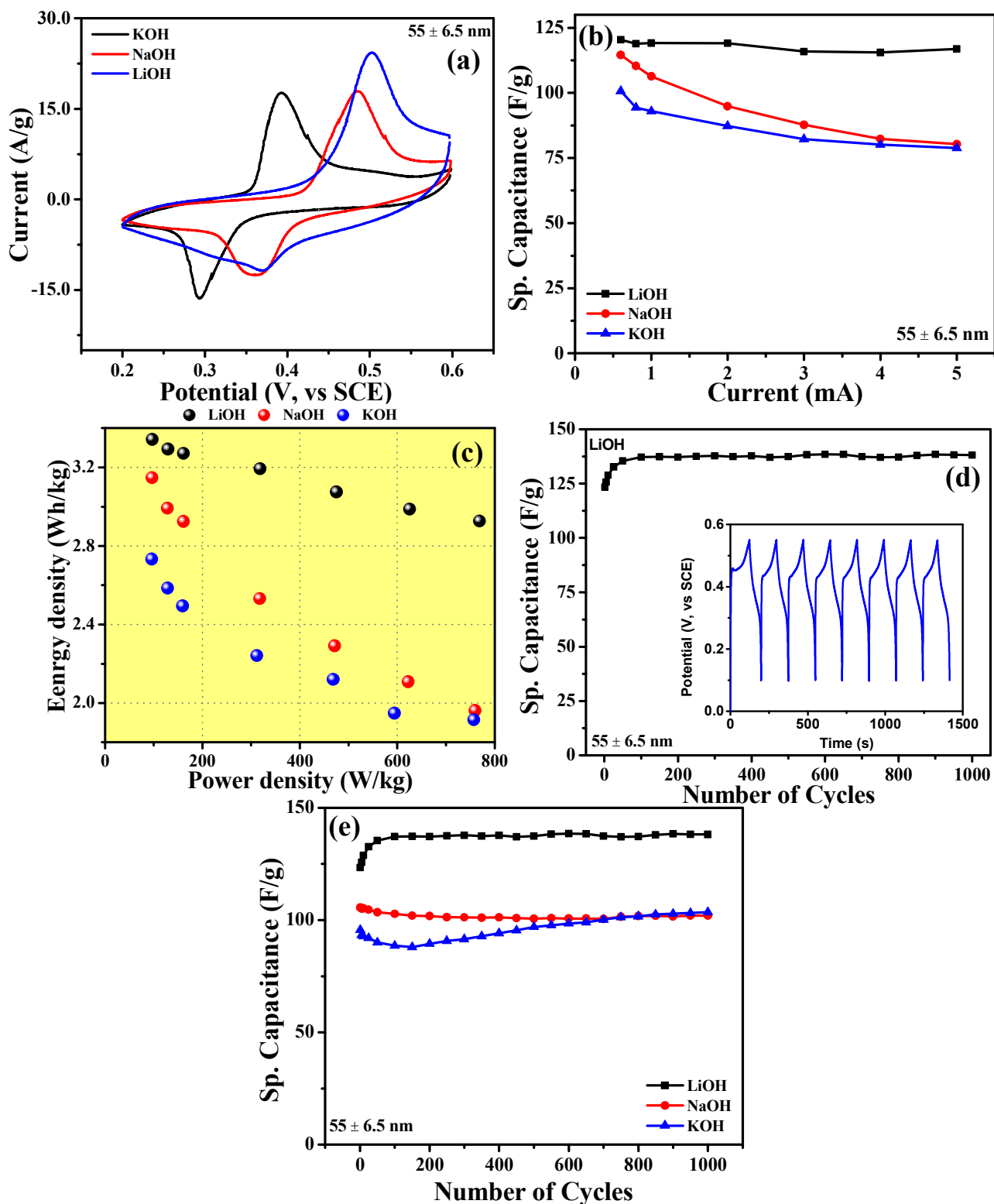


Figure 4. (a) Cyclic voltammogram curves of CuSbS₂ nanoplates using different electrolytes. (b) Variation of specific capacitance of CuSbS₂ nanoplates with applied current in different electrolytes. (c) Ragone plot for different thickness nanoplates. (d) Cycling performance of the CuSbS₂ nanoplates at a constant current of 0.5 mA using LiOH electrolyte. The inset shows the first few cycles of the charge-discharge curves. (e) Cycling performance of 55 ± 6.5 nm CuSbS₂ nanoplates at a constant current of 0.5 mA using different electrolytes.

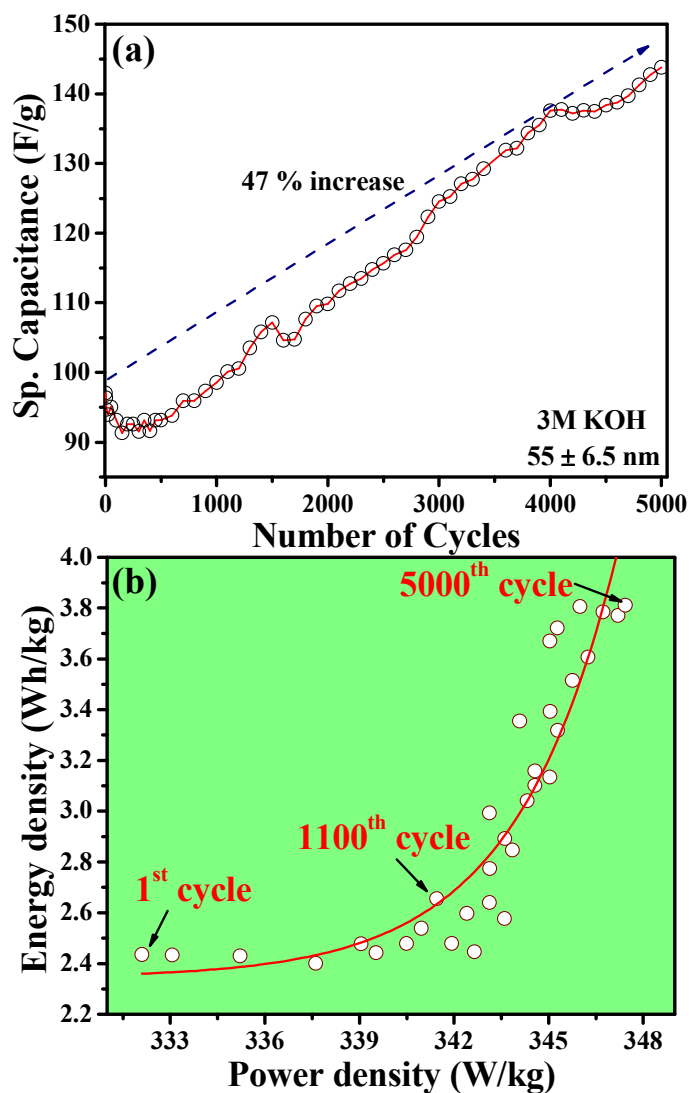


Figure 5. (a) Cycling performance of the CuSbS₂ nanoplates at a constant current of 0.5 mA using KOH electrolyte up to 5000 cycles. (b) Ragone plot showing variations of energy density and power density with respect to number of cycles.

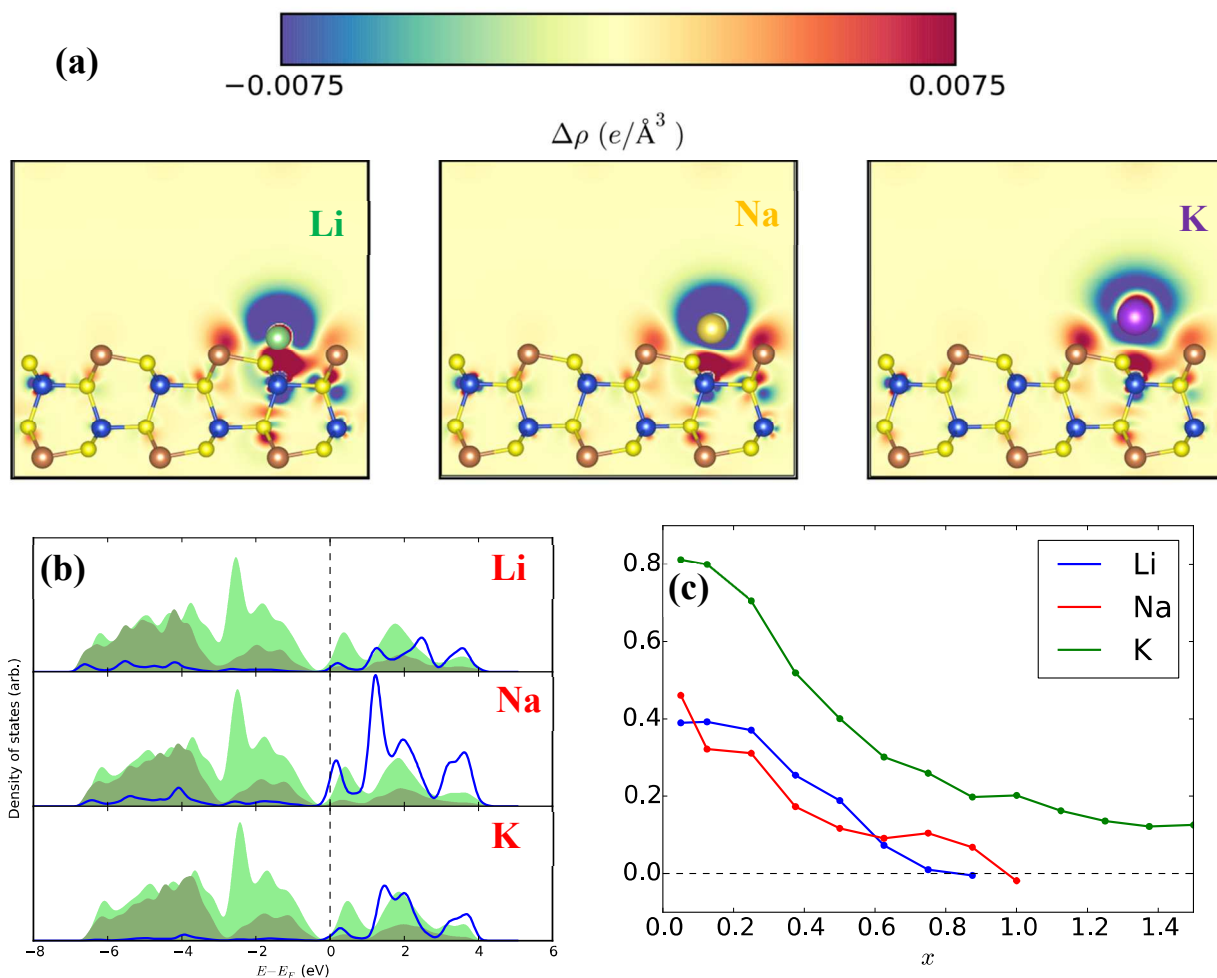


Figure 6. (a) Valence charge density for Li, Na, and K adsorbates with respect to the charge density of non-interacting species, nonbonded density, plotted in the plane of the adsorbed ion. Cu sites are blue, Sb are orange, and S are yellow, (b) Partial density of states projected onto Li, Na, K (bottom) valence $(n-1)s$ orbitals (blue line), compared to the total (light green) and S-projected (dark green) DOS. The ionic ns orbital is nearly empty in all cases and shows some hybridization with the valence S $3p$ bands. (c) OCV v. x for Li (blue), Na (red), and K (green) adsorption. $x = 0.5$ corresponds to complete monolayer coverage of the Cu sites. Higher x gives coverage of S (until $x = 1.0$) and Sb sites on a single side.

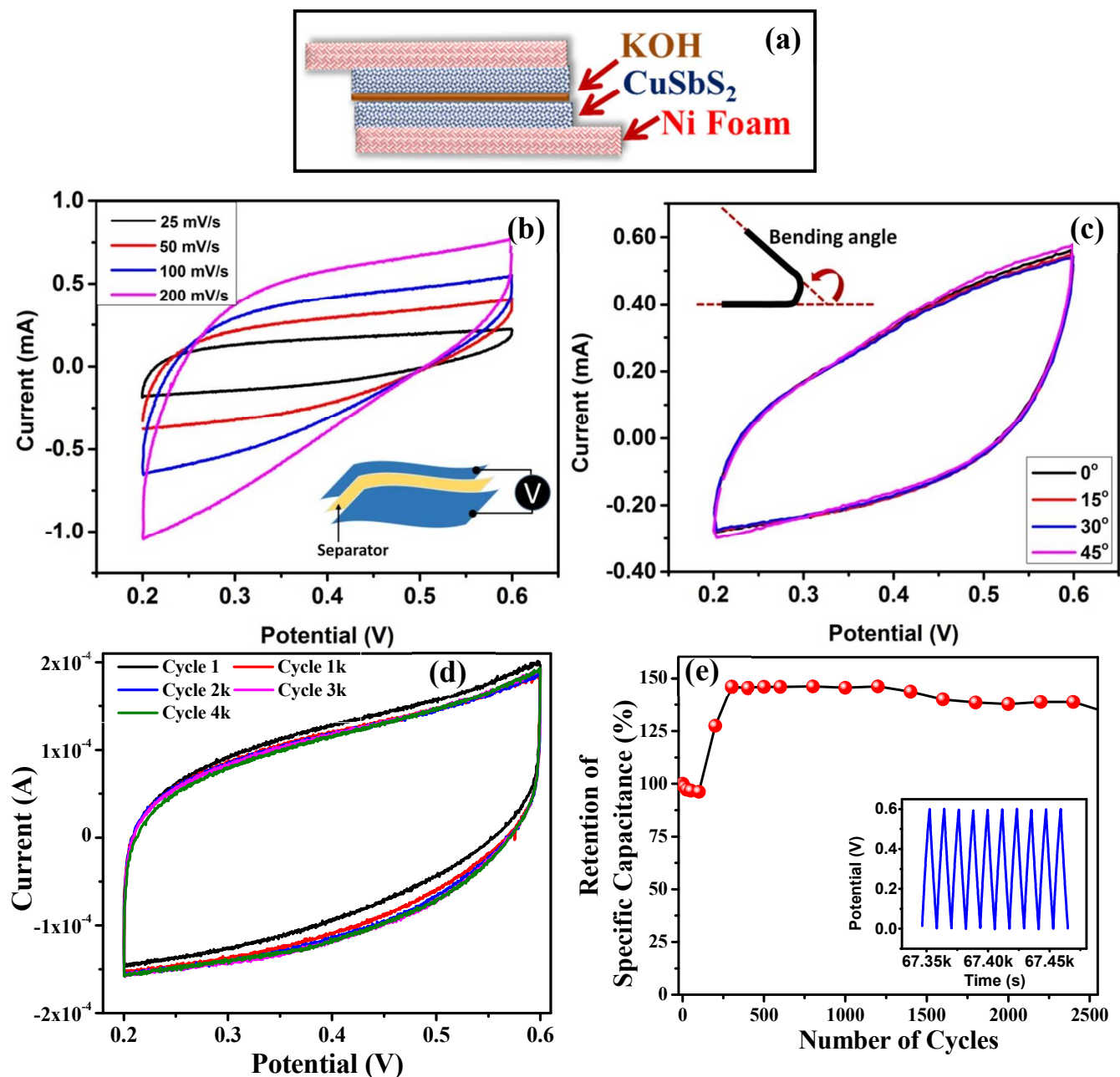


Figure 7. (a) Schematic of flexible quasi-solid-state supercapacitor device fabricated using 55 ± 6.5 nm CuSbS₂ nanoplates. (b) Cyclic voltammogram curves of CuSbS₂ nanoplates supercapacitor device at different scan rates using KOH. (c) Cyclic voltammogram curves of CuSbS₂ nanoplate supercapacitor device at different bending angles. (d) Cyclic voltammogram curves showing cyclic stability of CuSbS₂ nanoplates device. (e) Cycling performance of the CuSbS₂ nanoplates supercapacitor device at a constant current of 1 mA. The inset shows the first few cycles of the charge-discharge curves.

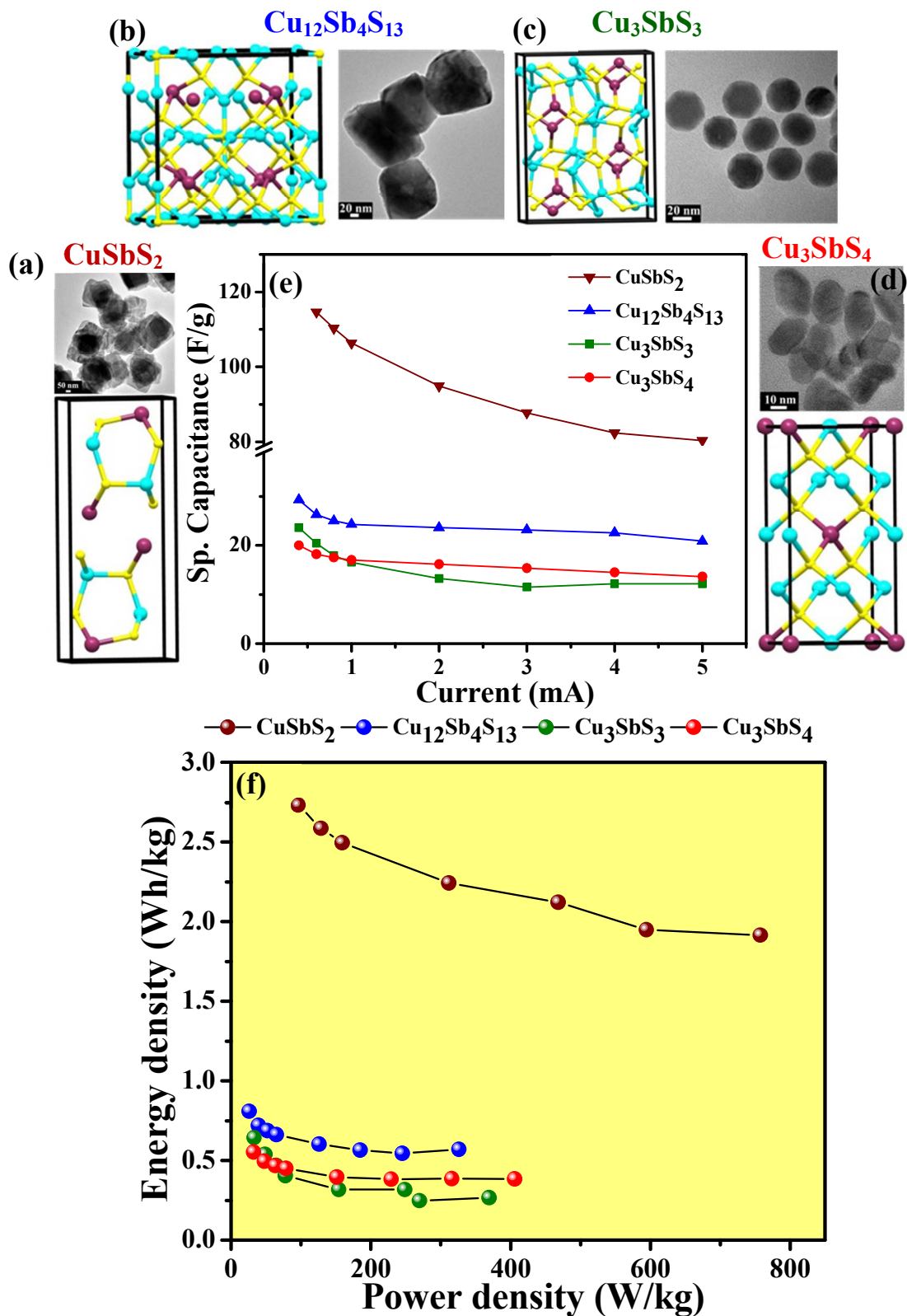


Figure 8. (a)-(d) Crystal structure and TEM images of different phases of Cu-Sb-S. (e) Variation of specific capacitance of different phases of Cu-Sb-S nanocrystals with applied current. (f) Ragone plot showing energy density vs power density for the different Cu-Sb-S phases.

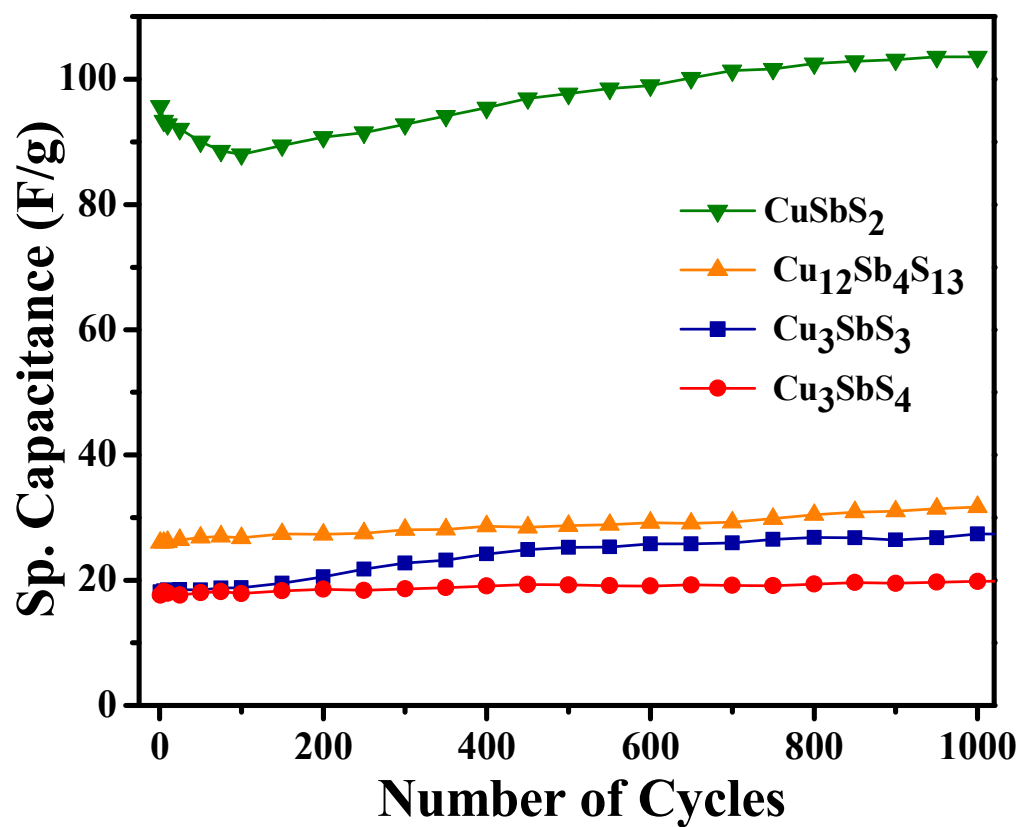


Figure 9. (a) Cycling performance of nanocrystals of CuSbS₂, Cu₁₂Sb₄S₁₃, Cu₃SbS₃ and Cu₃SbS₄ using KOH

“Graphical Abstract”

Supercapacitor devices using nanoplates of ternary layered sulfide CuSbS_2 exhibit very good performance with excellent cyclic stability, flexibility and can be operated over a wide temperature range.

