Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Hollow Heterostructured $Cu_{1.96}S$/NiS Microspheres Coupled with Nitrogen/Sulfur Dual-Doped Carbon Realizing Superior Reaction Kinetics and Sodium Storage

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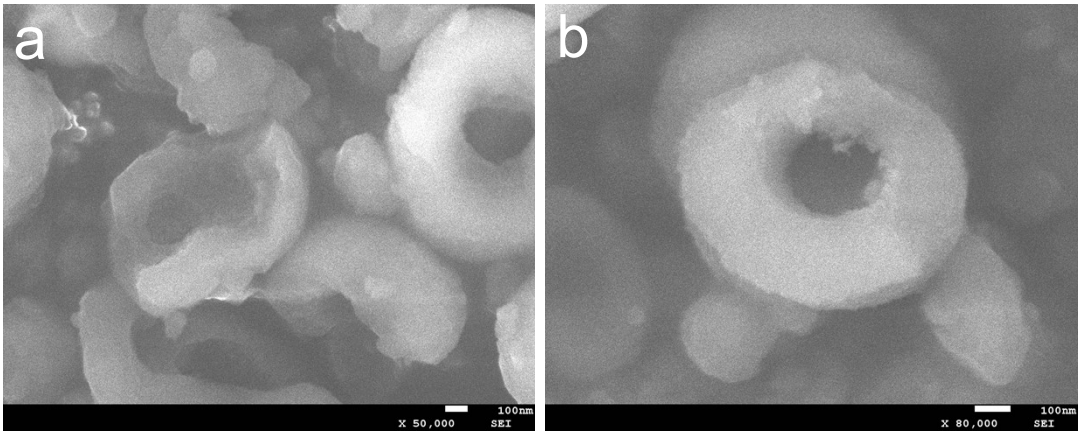

Fig. S1 (a) Low- and (b) high-magnification SEM images of damaged CuNi-G microspheres.

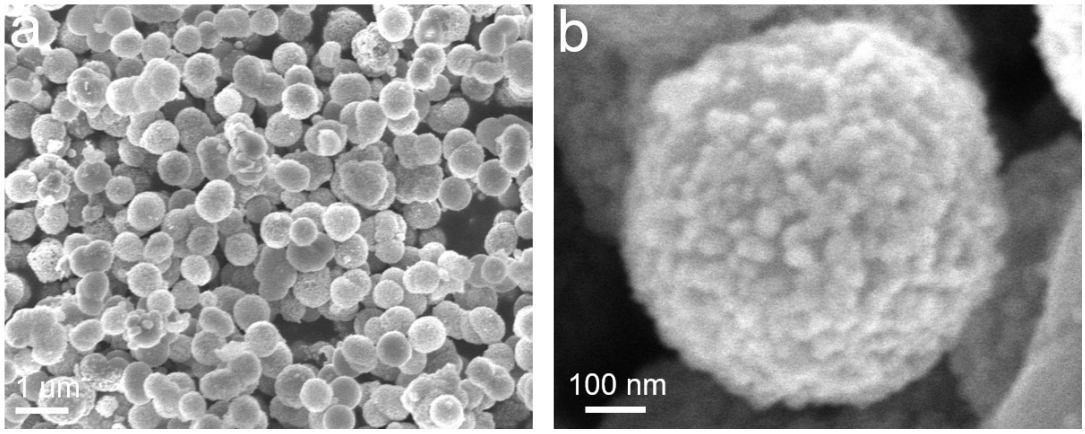

Fig. S2 (a) Low- and (b) high-magnification SEM images of $Cu_{1.96}S$/NiS microspheres.

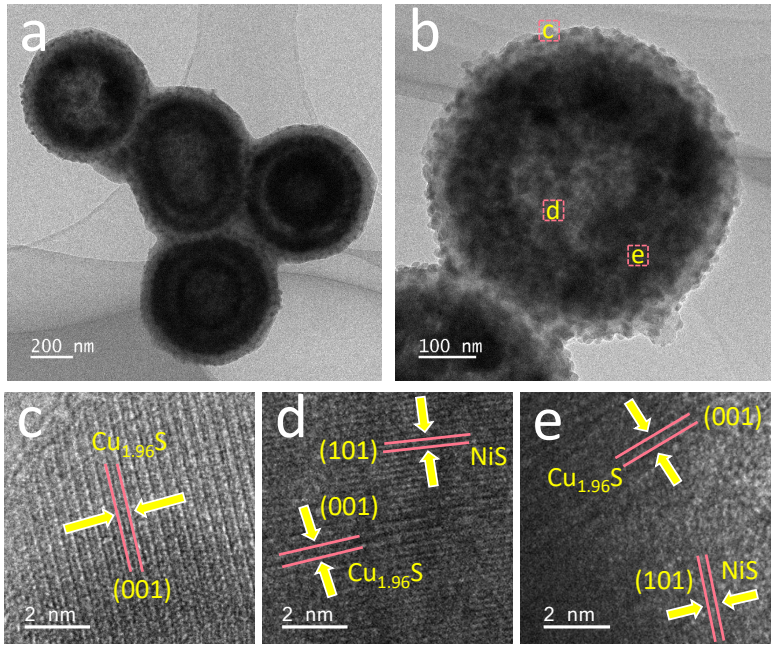

Fig. S3 (a, b) TEM of $Cu_{1.96}S$/NiS@DC microspheres; (c-e) HRTEM images captured from the wall edge of $Cu_{1.96}S$/NiS@DC shown in (b).

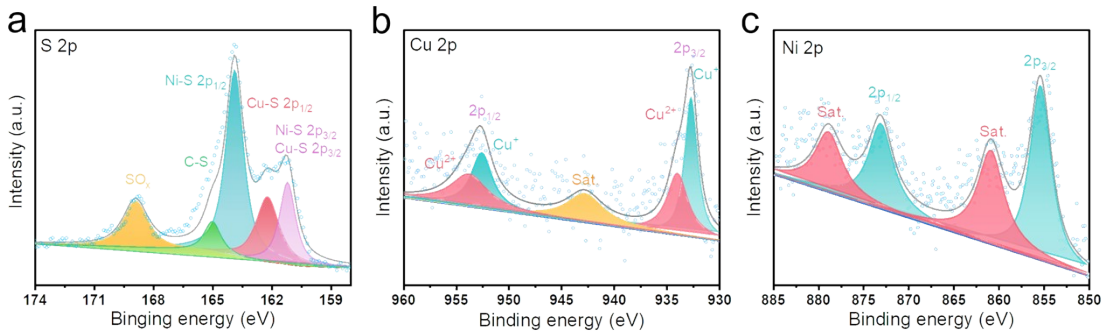

Fig. S4 The high-resolution XPS spectra of (a) S 2p, (b) Cu 2p, and (c) Ni 2p of $Cu_{1.96}S$/NiS microspheres.

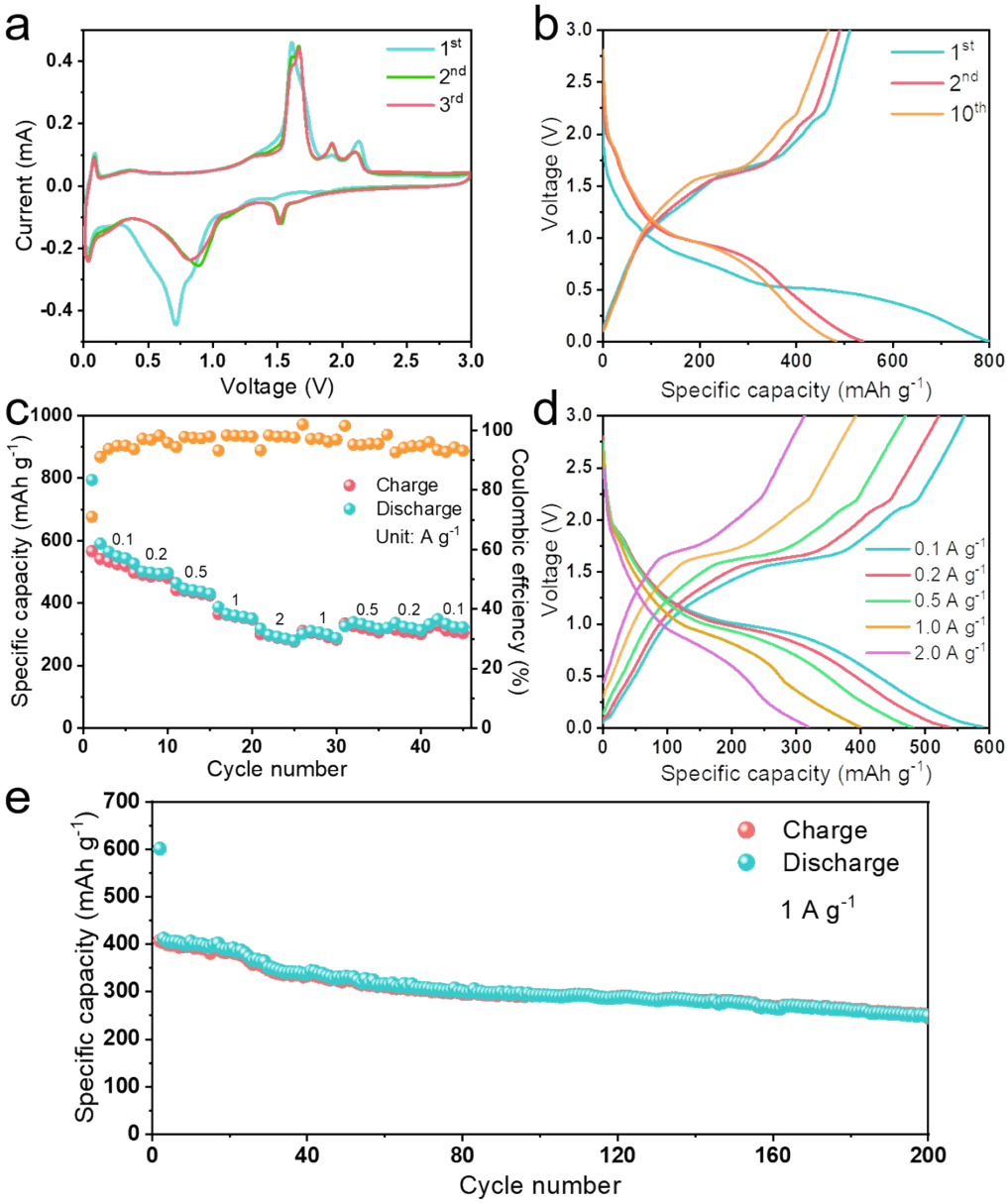

Fig. S5 Electrochemical performance of $Cu_{1.96}S$/NiS electrode. (a) CV curves at 0.1 mV s^{-1} in the voltage range of 0.01-3.0 V. (b) Galvanostatic charge-discharge voltage profiles at 0.2 A g^{-1}. (c) Rate performance and Coulombic efficiency ranging from 0.1 to 2.0 A g^{-1}. (d) Voltage profiles at various current densities. (e) Prolonged cycle life and Coulombic efficiency at 1.0 A g^{-1}.

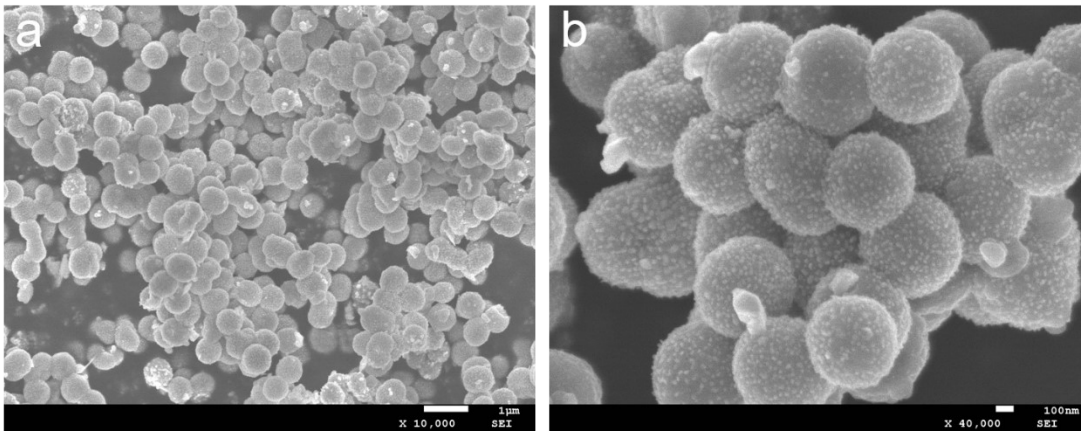

Fig. S6 (a) Low- and (b) high-magnification SEM images of L-$Cu_{1.96}S$/NiS@DC microspheres.

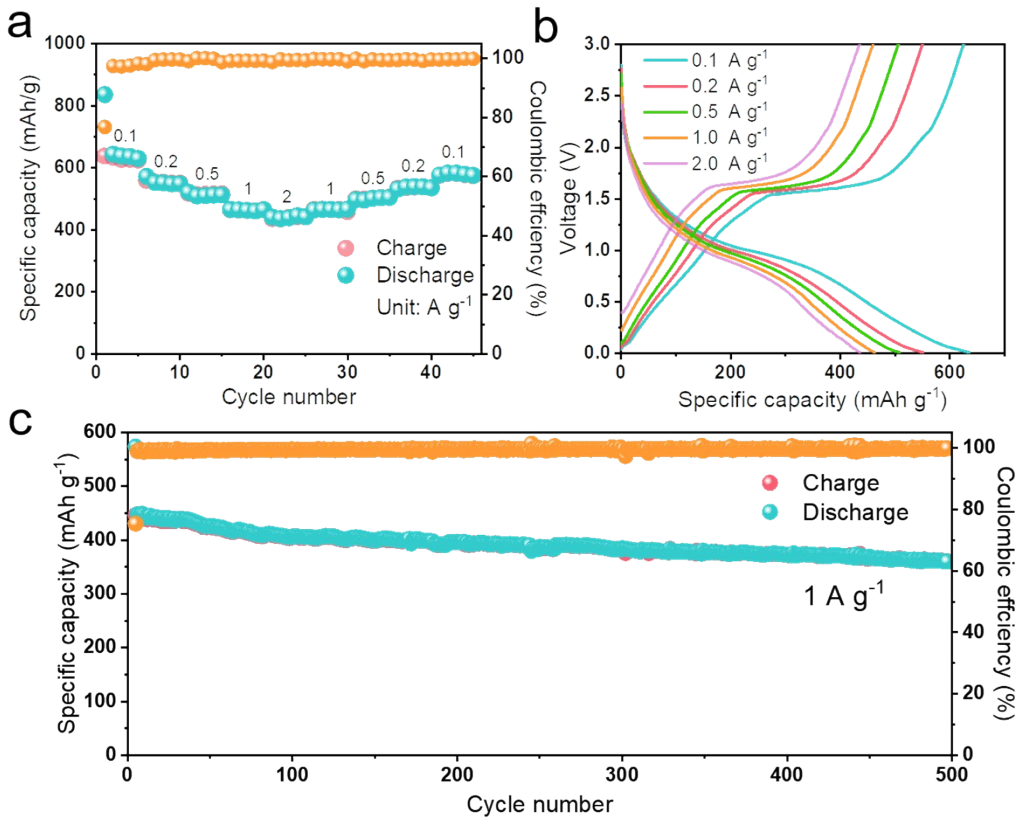

Fig. S7 Electrochemical performance of L-$Cu_{1.96}S$/NiS@DC electrode. (a) Rate performance and Coulombic efficiency ranging from 0.1 to 2.0 A g^{-1}. (b) Voltage profiles at various current densities. (c) Prolonged cycle life and Coulombic efficiency at 1.0 A g^{-1}.

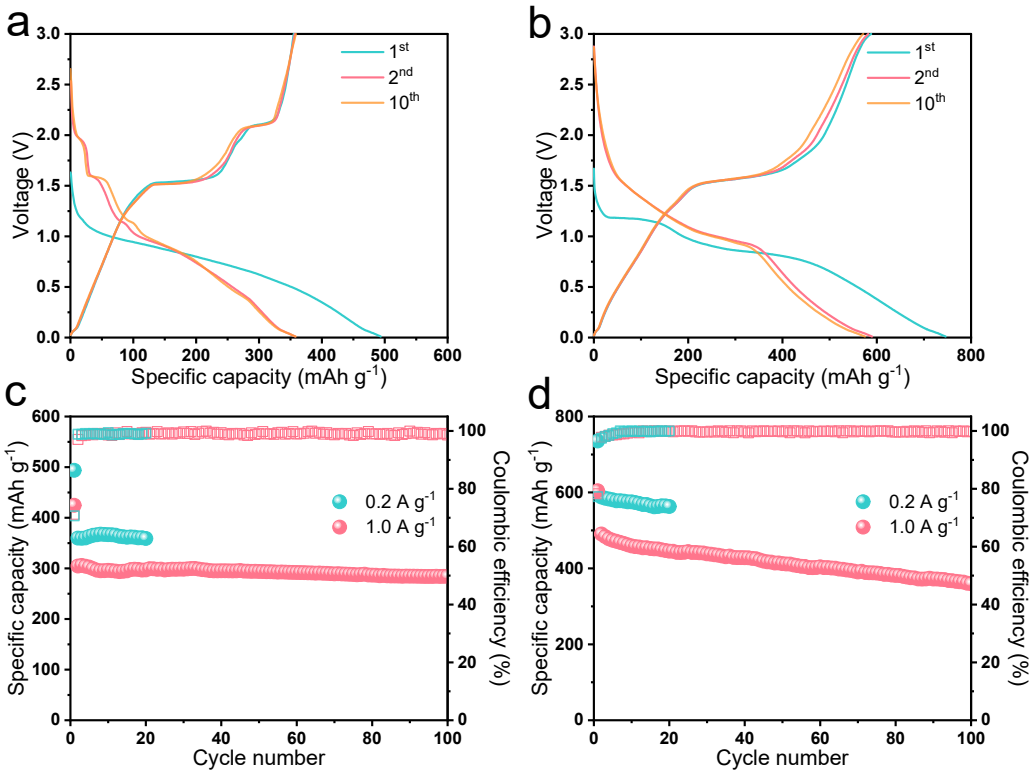

Fig. S8 Galvanostatic charge-discharge voltage profiles of the carbon-coated (a) $Cu_{1.96}S$ and (b) NiS electrodes at 0.2 A g^{-1}. Cycle life and Coulombic efficiency of the carbon-coated (c) $Cu_{1.96}S$ and (d) NiS electrodes at 0.2 A g^{-1} and 1.0 A g^{-1}.

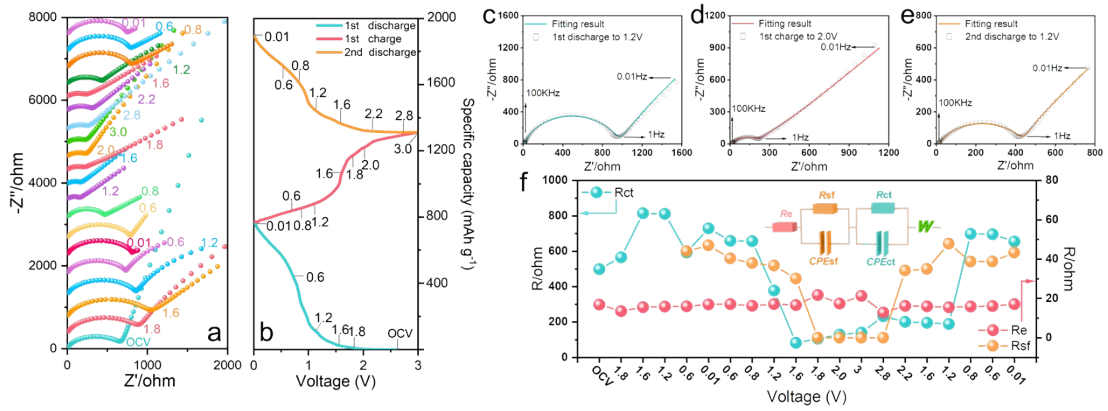

Fig. S9 Electrochemical reaction kinetics of $Cu_{1.96}S$/NiS electrode. (a) Nyquist plots collected at each point marked in (b) in the frequency range of 100 kHz to 10 mHz. (b) Discharge-charge profiles: each point represents an EIS measurement. Typical Nyquist plots collected at the (c) 1st discharge to 1.2 V, (d) 1st charge 2.0 V, and (e) 2nd discharge to 1.2 V. (f) EIS parameters derived from the equivalent circuit (inset of f).

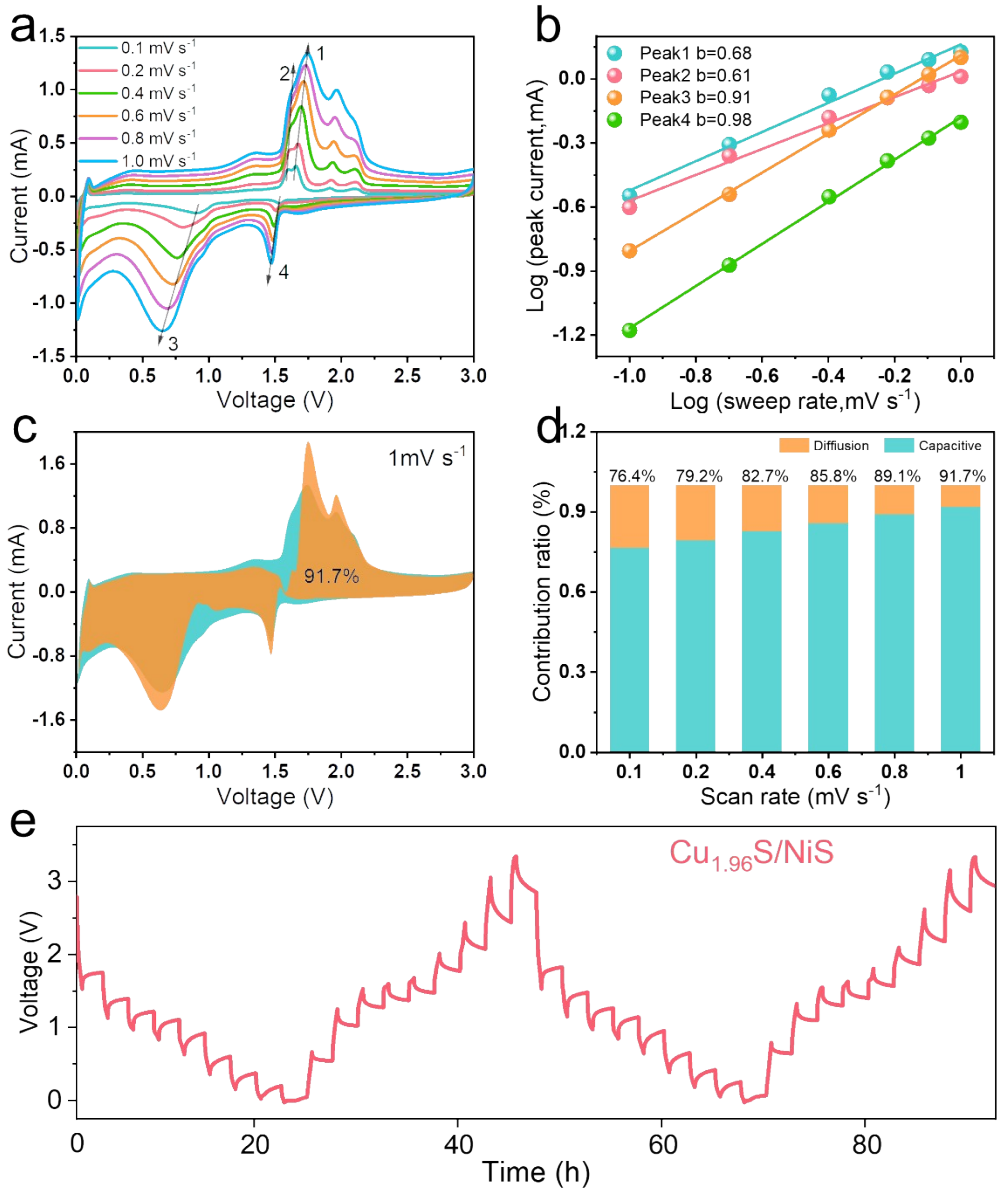

Fig. S10 Electrochemical reaction kinetics of $Cu_{1.96}S$/NiS electrode. (a) CV curves at various scan rates from 0.1 to 1.0 mV s^{-1}. (b) Determination of the b value using the relationship between peak current and scan rate. (c) Separation of the capacitive and diffusion currents at a scan rate of 1.0 mV s^{-1} with the capacitive fraction shown by the shaded region. (d) Contribution ratio of the capacitive and diffusion-controlled charge versus scan rate. (e) GITT curves.

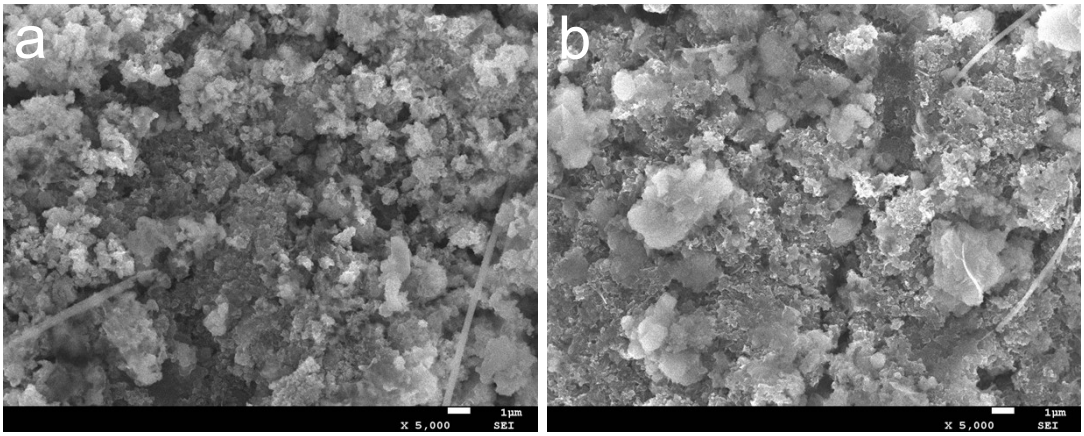

Fig. S11 SEM images of (a) $Cu_{1.96}S$/NiS and (b) $Cu_{1.96}S$/NiS@DC electrodes after 1000 cycles at 1.0 A g^{-1}.

Table. S1 The atomic ratio of Cu and Ni in the obtained materials.

	$Cu_{1.96}S$/NiS@DC	**L-$Cu_{1.96}S$/NiS@DC**
Cu : Ni	0.94 : 1	0.39 : 1

Table S2 Electrochemical performances of $Cu_{1.96}S$/NiS@DC compared with other previously-reported bimetallic sulfides based anode materials for SIBs.

Bimetallic Sulfides	**Voltage window [V vs. Na^+]**	**Current density**	**Capacity retention (%)**	**Rate capacity (mAh g^{-1}) / current density**	**Ref.**
SnS_2@MoS_2@rGO	0.01-3.0	0.1 A g^{-1}	92.5 (after 100 cycles)	408 at 0.2 A g^{-1} 346 at 0.8 A g^{-1}	1
Cu_2S@ZnS/C	0.4-2.6	0.2 A g^{-1}	98.1 (after 200 cycles)	424 at 0.2 A g^{-1} 415 at 1 A g^{-1}	2
ZnS@NC@MoS_2	0.01-2.5	1 A g^{-1}	81.4 (after 120 cycles)	461.4 at 0.1 A g^{-1} 354.6 at 1 A g^{-1}	3
NiS/MoS_2/C	0.01–3.0	1 A g^{-1}	70.5 (after 200 cycles)	516 at 0.1 A g^{-1} 444 at 1 A g^{-1}	4
Ni_3S_2/Co_9S_8/NC	0.1-3.0	0.1 A g^{-1}	92 (after 300 cycles)	405.2 at 0.1 A g^{-1} 347.8 at 1 A g^{-1}	5
SnS_2/FeS_2/rGO	0.01-3.0	1 A g^{-1}	85.7 (after 500 cycles)	682.8 at 0.2 A g^{-1} 449.7 at 1 A g^{-1}	6
MnS-FeS_2@NSC	0.01-3.0	0.1 A g^{-1}	80.1 (after 800 cycles)	342.7 at 0.2 A g^{-1} 266.6 at 1 A g^{-1}	7
Cu-CoS_2@Cu_xS	0.4-2.6	0.3 A g^{-1}	76 (after 300cycles)	446 at 0.2 A g^{-1} 368 at 1 A g^{-1}	8

SnS_2-CoS_2@C	0.01-2.5	0.1 A g^{-1}	99 (after 70 cycles)	625 at 0.1 A g^{-1} 425.1 at 1.0 A g^{-1}	9
FeS_2/MoS_2-rGO	0.01-3.0	0.1 A g^{-1}	90.1 (after 150 cycles)	432.5 at 0.1 A g^{-1} 406 at 1 A g^{-1}	10
$Fe_{1-x}S$/MnS	0.01-2.5	0.1A g^{-1}	81.4 (after 100 cycles)	561 at 0.05 A g^{-1} 350 at 1 A g^{-1}	11
CuS/FeS_2@NC	0.01-3.0	0.2A g^{-1}	99.1 (after 300 cycles)	575 at 1 A g^{-1} 608 at 0.2 A g^{-1}	12
$Cu_{1.96}S$/NiS@DC	0.01-3.0	0.2 A g^{-1} 1.0 A g^{-1}	95.8 (after 140 cycles) 89.1 (after 1000 cycles)	546.5 at 0.2 A g^{-1} 466.0 at 1 A g^{-1}	This work

Table S3 Fitting parameters of $Cu_{1.96}S$/NiS@DC charged to 2.0 V in the 1st cycle.

Electrolyte	R_e	8.865 Ω
SEI	R_{sf}	12.98 Ω
	CPE_{sf}-T	6.769E-5
	CPE_{sf}-P	0.7561
Charge transfer	R_{ct}	42.1 Ω
	CPE_{ct}-T	7.119E-5
	CPE_{ct}-P	0.6162
Diffusion	R_d of W_{dif}	406.8 Ω
	T of W_{dif}	2.156
	P of W_{dif}	1.237

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