Cu_2Se with Facile Synthesis as Cathode Material for Rechargeable Sodium Battery

Ji-Li Yue, Qian Sun, Zheng-Wen Fu*

Shanghai Key Laboratory of Molecular Catalysts and Innovative Materials, Department of Chemistry & Laser Chemistry Institute, Fudan University, Shanghai 200433, China. Fax: (+86)21-65642777; Tel: (+86)-21-65642522; E-mail: zwfu@fudan.edu.cn

Electronic Supplementary Information (ESI)

Materials Synthesis

Cu_2Se electrode was fabricated by reactions of evaporating selenium with copper grid at 400 ^oC for 10min in argon atmosphere. The unreacted copper grid was used as current collector. The weight of Se in Cu_2Se is obtained by subtracting final and original copper grid with an electrobalance (BP 211D, Sartorius). The weight of the Cu_2Se was calculated according to stoichiometric amount. The The loading density is about 0.66 mg/cm^2, and the thickness of Cu_2Se film is estimated to be about 100nm based on itsdensity (density=6.86 g/cm^3)

Physical characterization

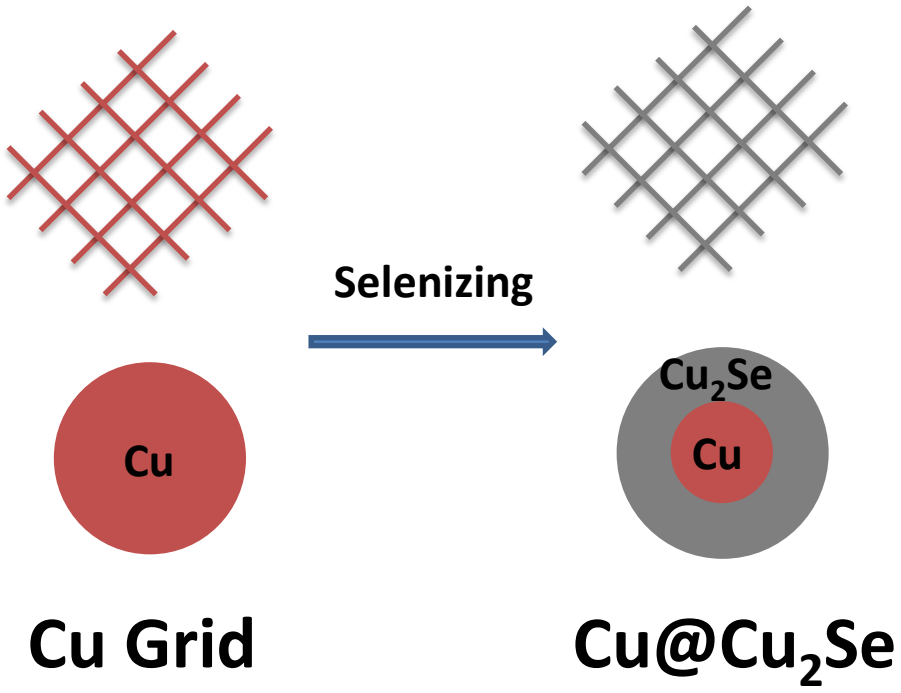
XRD patterns of samples were recorded by a Rigata/max-C diffractometer with Cu Kα radiation (λ=1.5406 Å) in 2θ scale between 20 and 60 ^{o} at scan rate of 2 ^{o} /min. TEM and SAED measurements were carried out in a 200 kV side entry JEOL 2010 TEM. The X-ray absorption data at the Cu K-edge of the samples were recorded at room temperature in transmission mode using ion chambers or in the fluorescent mode with silicon drift fluorescence detector at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a Si(111) double crystal monochromator. During the measurement, the synchrotron was operated at energy of 3.5GeV and a current between 150 and 210mA. The photon energy was calibrated with the first inflection point of Cu K-edge in Cu metal foil.

Electrochemical measurements

For the electrochemical measurements, the cells were constructed using the as-prepared as a working electrode and two sodium sheets as a counter and reference electrode, respectively. The electrolyte consisted of 1 M $NaClO_4$ (Alfa Aesar) in a nonaqueous solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1 (Shanshan Tech). The cells were assembled in an Ar filled glove box. Galvanostatic charge-discharge measurements were carried out at room temperature with a Land CT 2001A battery test system. The cells were cycled between 1.8V and 2.5V vs. Na^+/Na.

Potential step experiment

Potential step measurements are performed with CHI 660a electrochemical working station (CHI Instruments, TN) and have been described in previous works (Z.W. Fu and Q.Z. Qin, *J. Phys. Chem. B* 2000, **104**, 5505. In a typical method, when the potential at the Cu_2Se cathode was stepped from 2.5 V to 2.0 and 1.9V, respectively, the current (μA) variations with time (s) were recorded until the current reached a steady value.



Scheme S1. Schematic illustration of the preparation of Cu_2Se

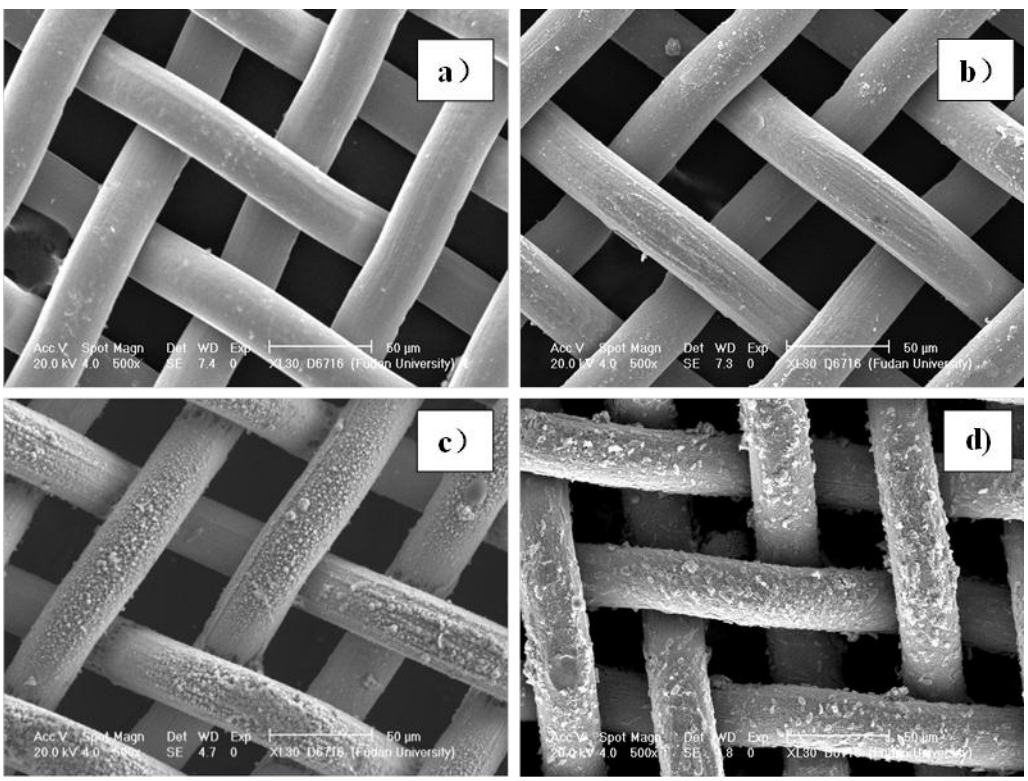
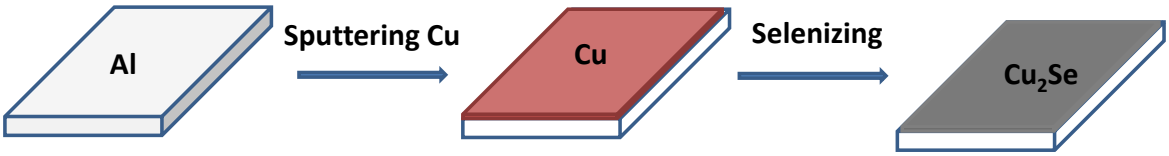


Figure S1. Scanning electron microscopy (SEM) images of (a) the Cu grid, (b) Selenizing, (c) Discharging to 1.8V, (d) Charging to 2.5V



Scheme S2. Schematic illustration of Samples which was used to XAS

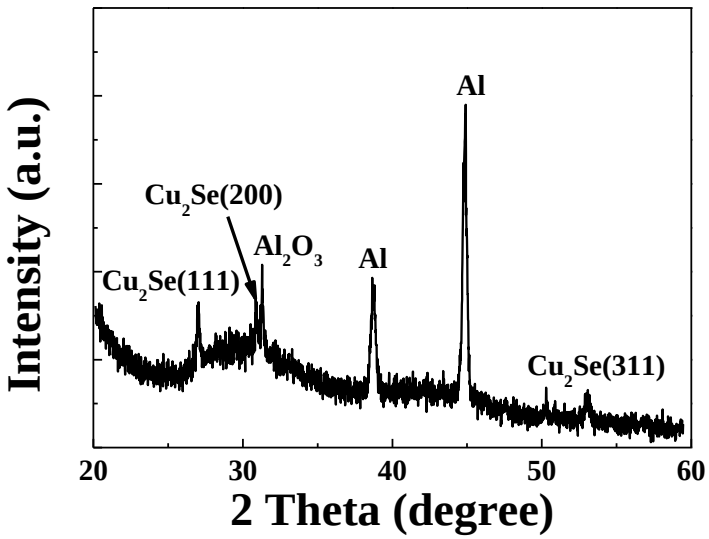


Figure S2. XRD patterns of Cu_2Se prepared on Al foil

Table S1 Sodium storage properties of Cu_2Se and other cathode materials reported recently.

Materials	Curve Shape	Discharge Plateau(Range) Voltage(V)	Discharge Capacity (mAh/g)	Energy density (Wh/kg)	Current Density	Reference
$Na_{0.74}CoO_2$	Slope	2.7-3.6	107	270	0.1C	1
$NaCrO_2$	Platform	2.9	110	319	0.05C	2
$NaVO_2$	Step	1.5,2.2	120	222	0.05C	5
$Na[Ni_{1/3}Fe_{1/3}Mn_{1/3}]O_2$	Slope	2.8-3.5	120	366	0.1C	3
$Na_{2/3}[Fe_{1/2}Mn_{1/2}]O_2$	Slope	1.5-4.3	190	551	0.05C	4
$Fe_2(MoO_4)_3$	Step	2.5,2.6	91	232	0.1C	6
$Na_3V_2(PO_4)_3$	Platform	3.4	98	333	0.05C	7
$KFe_2(CN)_6$	Step	2.9, 3.7	100	306	0.05C	8
$Na_{1.40}MnFe(CN)_6$	Platform	3.4	134	456	0.1C	9
$NaFeF_3$	Slope	1.5-4.5	170-180	410	0.01C	10
SeS_2	Slope	0.5-3.5	288	433	0.2C	11
$MoSe_2$	Slope	0.3-3	106	212	0.1C	12
V_2O_5	Slope	2.5-3.5	230	460	0.1C	15
Cu_2Se	Platform	1.9	253	488	0.1C	This work