Supporting Information for:

High Supercapacitor Electrode Performance of Cu_2ZnSnS_4 (CZTS) Thin Films Grown by ECD

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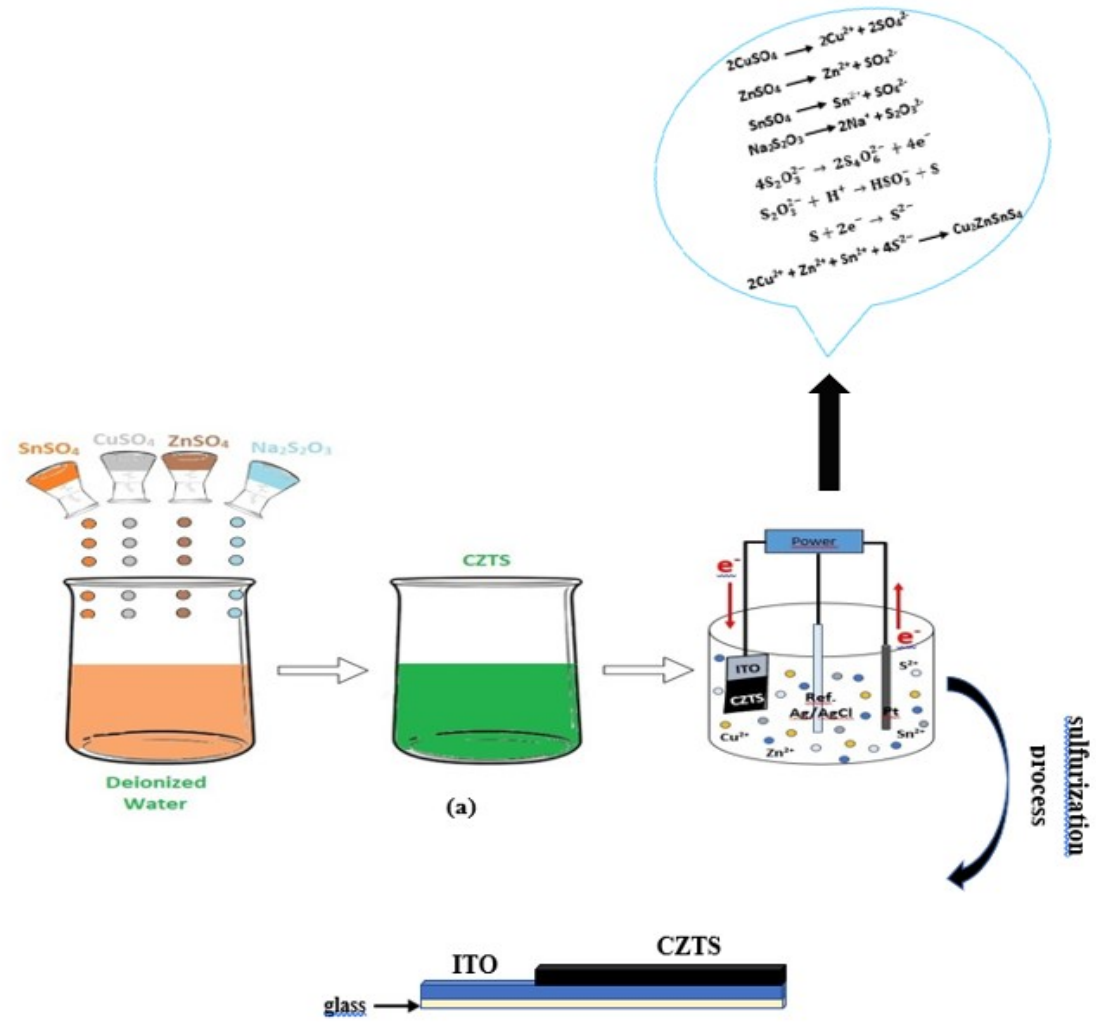

Fig. S1. Schematic presentation of CZTS TFs grown by ECD on ITO substrate at room temperature (b) A schematic illustration of the CZTS electrode deposited on an ITO substrate

Fig. S1(a) shows schematic procedure of CZTS TFs grown by ECD on ITO substrate. In a standard experimental setup, 50 mL of deionized water was used as the solvent for the following reagents: 0.02 M copper sulfate, 0.1 M zinc sulfate heptahydrate, 0.02 M tin sulphate, 0.02 M sodium thiosulphate, and 0.2 M sodium citrate tribasic. The solution was prepared while maintaining constant magnetic stirring. Before the deposition process, the ITO substrates were subjected to ultrasonic cleaning for five minutes in acetone, methanol, and trichloroethylene, in sequence. Following this, the substrates were rinsed with deionized water for five minutes and allowed to dry. After cleaning, the ITO films were annealed at 400°C for 30 minutes in a nitrogen atmosphere. The electrochemical deposition (ECD) technique was then utilized to deposit CZTS thin films onto the ITO-coated glass substrates at ambient temperature. Also, the experimental apparatus employed an Interface 1000 electrochemical workstation, which was integrated with a three-electrode system. In this configuration, an Ag/AgCl electrode was used as the reference electrode, a platinum (Pt) electrode served as the counter electrode, and an ITO-coated substrate functioned as the working electrode. All measurements and processes were conducted at room temperature, as depicted in Fig. S1(a). Table S1 presents the detailed electrochemical deposition parameters utilized for the growth of CZTS TFs on ITO-coated substrates. These parameters include key factors such as deposition time, applied voltage, solution composition, and temperature conditions, which were carefully controlled during the electrochemical process to achieve optimal film characteristics. The electrodeposition of Cu–Zn–Sn and sulfur species from a single solution presents a challenge due to the distinct oxidation and reduction potentials of their respective ions (Cu(II), Zn(II), Sn(IV), and Sn(II)). Therefore, Cyclic Voltammetry (CV) measurement was conducted with a scan rate of 50 mV/s, covering a potential range from 0 to -1.5 V, in a solution containing Cu, Zn, Sn, and S species, along with trisodium citrate before deposition [1]. Then, all depositions were carried out at room temperature under a cathodic potential of -1.05 V as given in table1[2]. The CZTS solution prepared at pH 5, was used for the growth of CZTS TFs and the growth process was carried out over a period of 2700 s using the experimental setup with a three-electrode system (as shown in Fig. 1(a)). The deposited films were extensively rinsed with deionized water and subsequently dried using a nitrogen gas flow. Then, the films were subjected to an annealing treatment at 580°C for one hour, in the presence of 0.5 g of sulfur powder, under a nitrogen atmosphere to perform the sulfurization process. Fig. S1(b) shows schematic presentation of the CZTS electrode electrodeposited on ITO substrate prepared for the electrochemical measurements.

Table S1. Deposition parameters of CZTS TFs electrodeposited on ITO substrate at room temperature

Deposition Parameters				
CIS/ITO	**Potential (V)**	**pH**	**Time (s)**	**Molarity**
As-deposited	**-1.05**	**5**	**2700**	0.02M $CuSO_4$ 0.01M $ZnSO_4.7H_2O$ 0.02M $SnSO_4$ 0.02M $Na_2S_2O_3$ 0.2M $Na_3C_6H_5O_7$

Table S2. The calculated results of 2θ, FWHM, d, and D of the CZTS TF obtained from XRD plot and the capacitance values obtained from CV at different scan rates

XRD data				
(hkl)	**Pos. (°2θ)**	**FWHM (°2θ)**	***d*-spacing (Å)**	**D (nm)**
(210)	26.78	0.197	3.326	75.56
(112)	28.95	0.162	3.082	92.32
(211)	38.38	0.454	2.343	33.77
(220)	47.75	0.270	1.903	58.65
(322)	54.55	0.340	1.681	47.92
(312)	56.60	0.348	1.625	47.26
CV data				
Scan rate (mV/s)	**Area**		**Capacitance (from CV) (F/g)**	
1	4.746×10^{-4}		1483	
5	6.18×10^{-4}		386	
10	6.01×10^{-4}		187	
25	9.52×10^{-4}		119	
50	1.45×10^{-4}		90	
100	2.36×10^{-4}		73	

Table S3. Comparison of the electrode materials' electrochemical properties performed on various substrates at different scan rates and current densities

Electrode	Specific Capacitance (Fg^{-1})	Current Density or scan rate	Deposition technique	Cycle numbers	Ref.
CZTS on ITO	1695	1 Ag^{-1}	ECD	5000	our work
CZTS/RGO	248.5	1 Ag^{-1}	hydro thermal	1000	[3]
CZTS/p-PDA nanocomposite	424.6	0.1 Ag^{-1}	chemical process	10000	[4]
CZTS/PANI nanocomposites	371	2.5 Ag^{-1}	an in-situ supercritical water reaction	1000	[5]
Cu_2ZnSnS_4 inks	1709	0.5 mV/s	chemical process	-	[6]
CZTS on glass substrate	165.04	1 Ag^{-1}	SILAR	1000	[7]
PANI:CZTS nanocomposites	311	0.1 Ag^{-1}	hydro thermal	10000	[8]
CZTS based carbon nanocomposities	171	0.5 mV/s	chemical	3000	[9]

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