Electronic Supplementary Information (ESI)

Graphene boosted Cu_2GeS_3 for advanced lithium-ion battery

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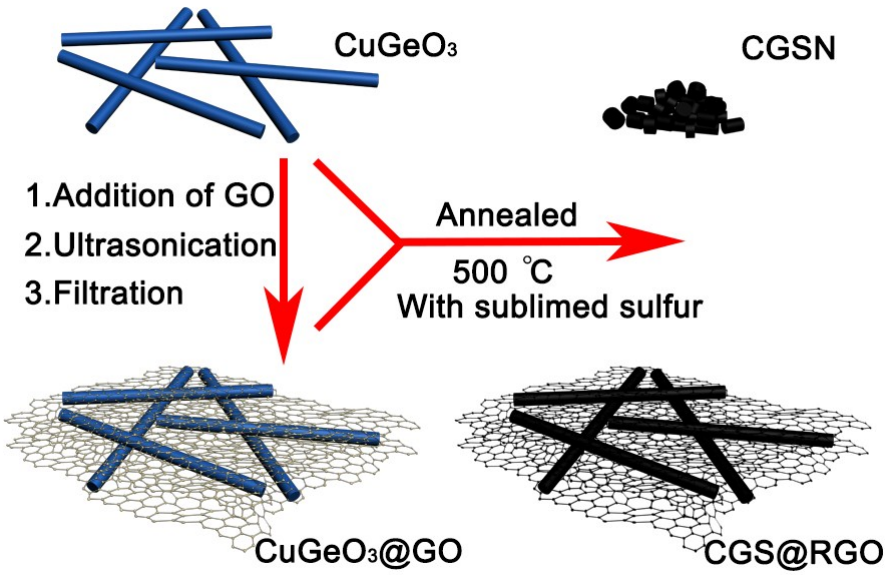

Fig. S1 Schematic diagram for the preparation process of CGSN and CGS@RGO, respectively.

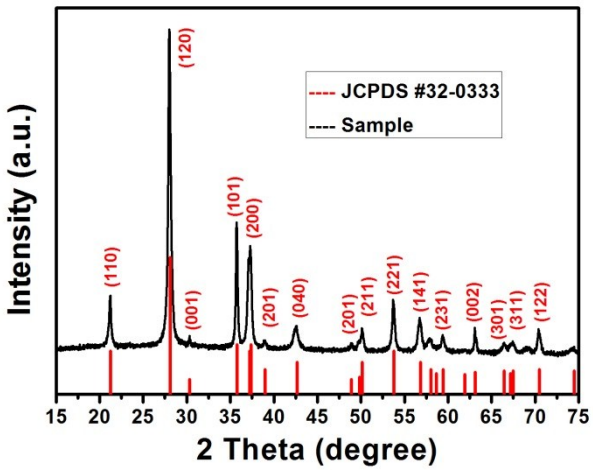

Fig. S2 XRD pattern of the $CuGeO_3$.

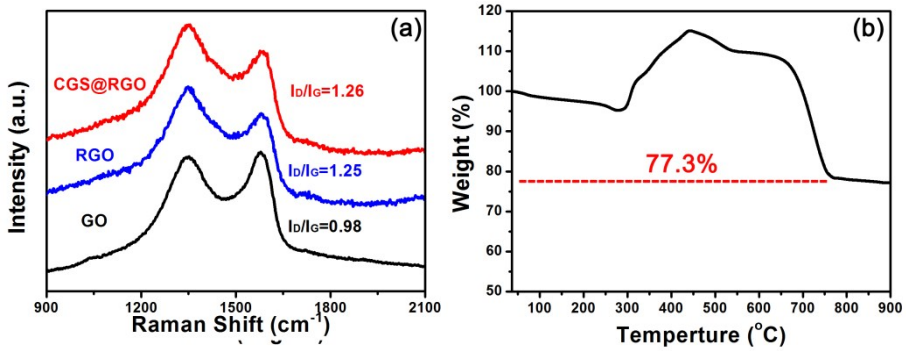

Fig. S3 (a) Raman spectra of GO, RGO and CGS@RGO. (b) TGA curve of the CGS@RGO.

Fig. S3b shows the TGA curve of CGS@RGO and similar phenomenon was reported in the previous study of graphene–metal sulfide composites.[1] The weight loss rate of graphene content is calculated based on the Cu_2GeS_3 and graphene and the residual products only include CuO and GeO_2.

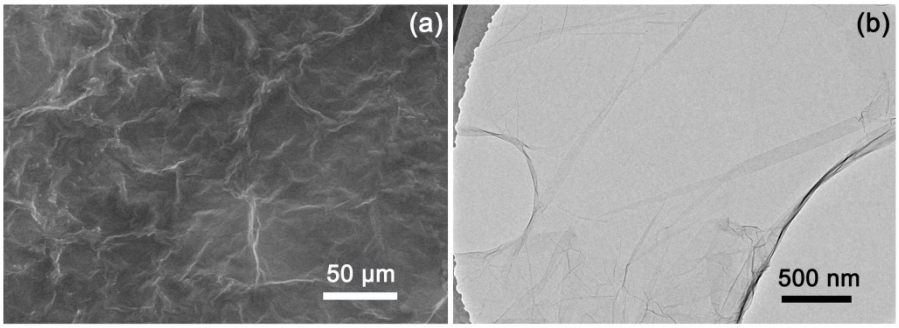

Fig. S4 (a) SEM and (b) TEM images of the RGO.

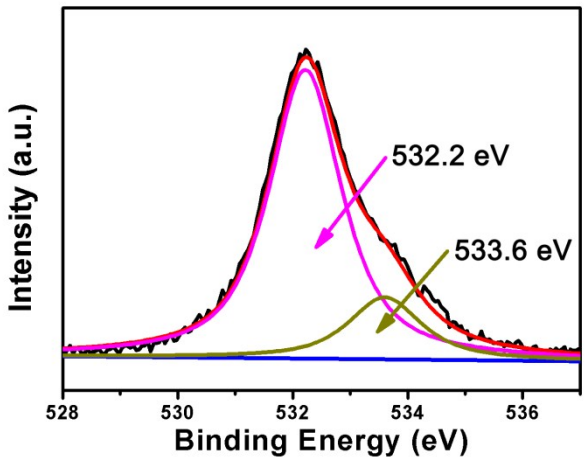

Fig. S5 High-resolution XPS spectra of O 1S in the CGS@RGO composite.

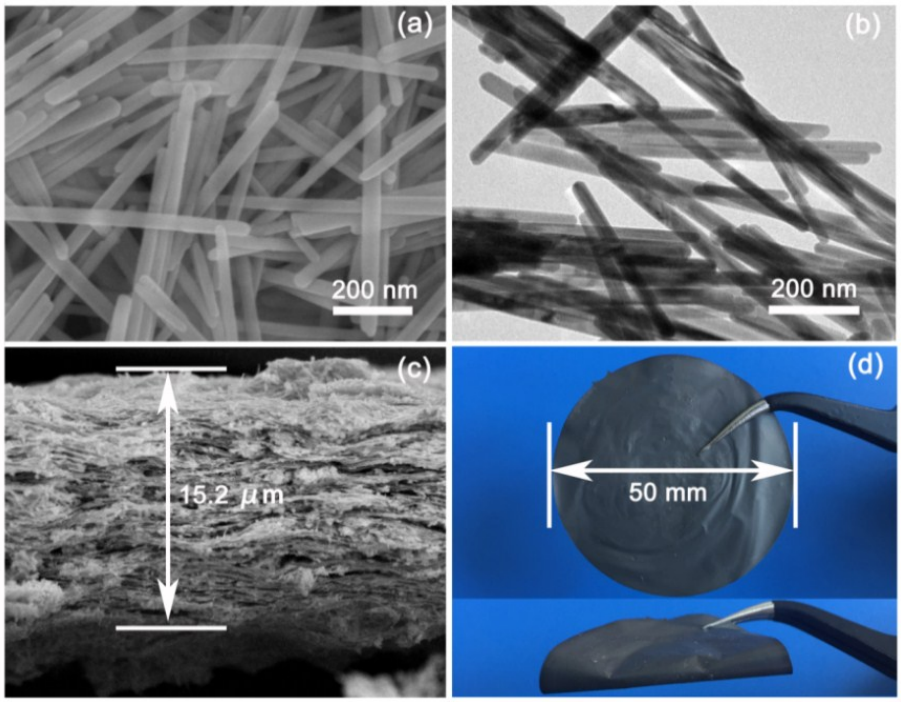

Fig. S6 (a) SEM and (b) TEM images of $CuGeO_3$. (c) The cross-sectional images and (d) digital photograph of CGS@RGO.

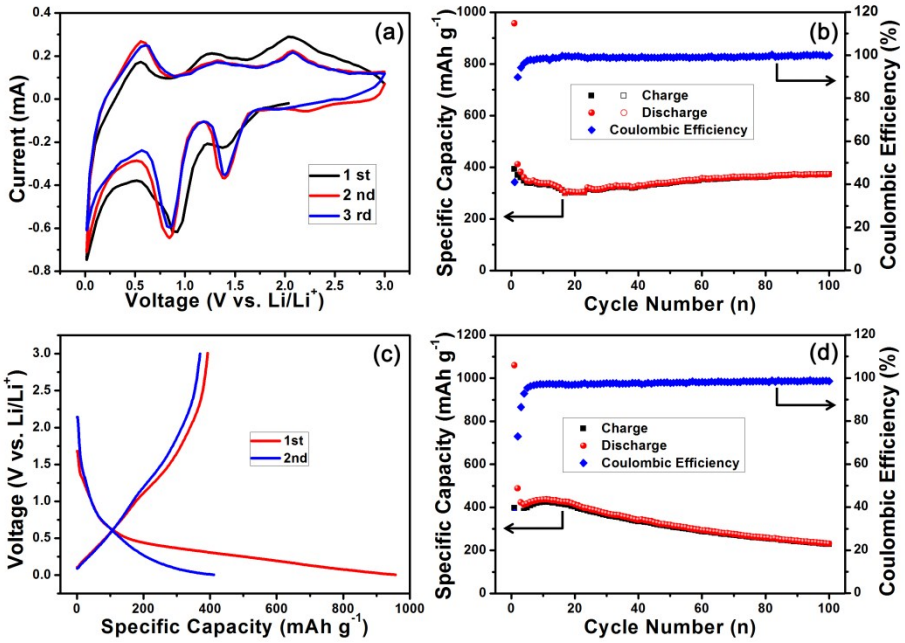

Fig. S7 (a) Cyclic voltammetry of the CGS@RGO at a scanning rate of 0.2 mV s^{-1}. (b)The cycling performance and (c) the initial two charge and discharge curves of the RGO electrode at a current density of 1000 mA g^{-1}. (d) The cycling performance of the $CuGeO_3$ electrode at a current density of 1000 mA g^{-1}.

The RGO was prepared by direct annealing GO with sublimed sulfur in argon atmosphere at 500 °C for 4 h. The RGO of CGS@RGO only offers a low capacity (about 50 mAh g^{-1} based on 13.5% RGO in the CGS@RGO) at a current density of 1000 mA g^{-1} as shown in Fig. S7b.

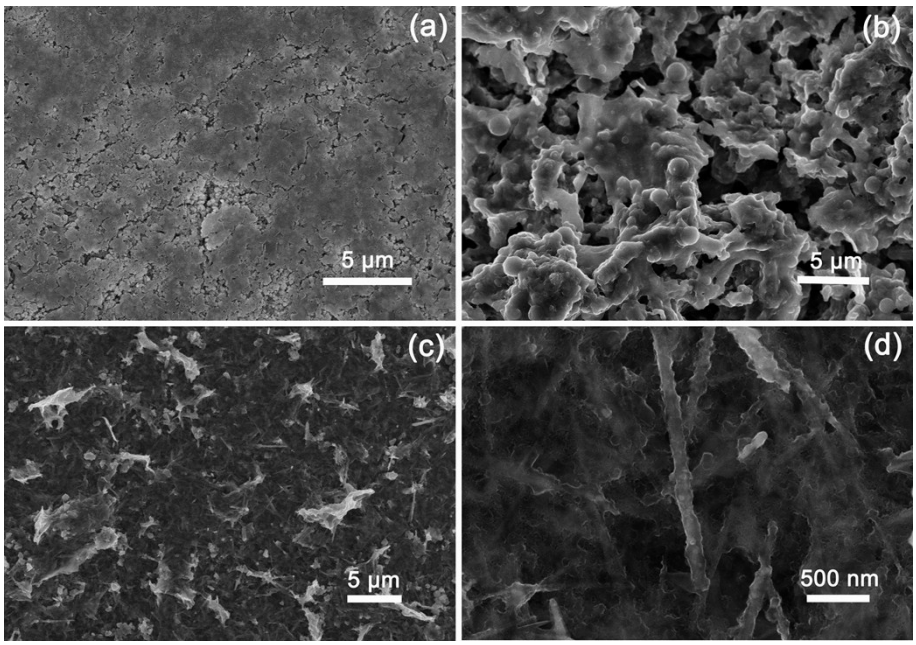

Fig. S8. SEM images of the CGSN electrode (a) before cycling and (b) after 10 charge/discharge cycles. (c, d) SEM images of the CGS@RGO electrode after 10 charge/discharge cycles.

Table S1. Comparison of CGS@RGO electrodes with those in previously published Cu-Ge-based anodes of LIBs.

electrodes	Current density	Charge specific capacity (mA h g^{-1})				
		1st	20th	50th	100th	200th
CGS@RGO (this work)	1000 mA g^{-1}	853.1	602	592	580	538
$CuGeO_3$[2]	150 mA g^{-1}	927	*N/A*	690	*N/A*	*N/A*
$CuGeO_3$-graphene[3]	200 mA g^{-1}	1265	*N/A*	853	*N/A*	*N/A*
	400 mA g^{-1}	~1050	*N/A*	448	*N/A*	*N/A*
$Cu_3Ge/GeO_x/CuGeO_3$[4]	200 mA g^{-1}	971	645	*N/A*	*N/A*	*N/A*
Cu_3Ge/Ge@ graphene [5]	1C	*N/A*	*N/A*	*N/A*	790	*N/A*
$Cu_xGeO_y/Cu/C$[6]	150 mA g^{-1}	~1005	*N/A*	*N/A*	~900	*N/A*
$Cu_3Ge/Ge/C$[7]	0.5C	1352	*N/A*	*N/A*	*N/A*	~1345
$GeO_2/Cu/C$[8]	0.2C	869	*N/A*	*N/A*	695	*N/A*

In the table S1, the capacity of $Cu_3Ge/Ge/C$ (ref. 7) is based on active Ge content in the $Cu_3Ge/Ge/C$ composites, which does not include the Ge present in the Cu_3Ge content.[7]

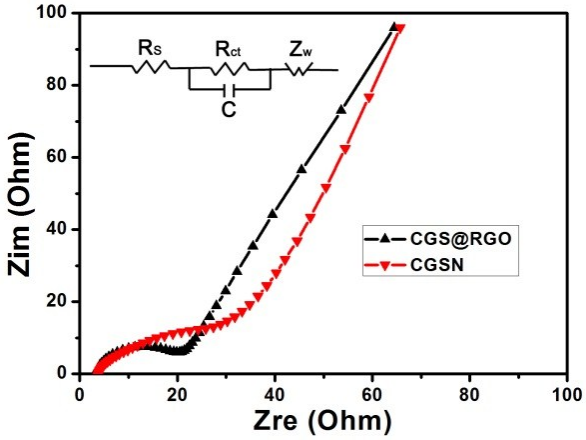

Fig. S9 EIS curves of the CGS@rGO and CGSN electrode before cycling and the inset equivalent circuit to fit the EIS. The Rs, Rct, C and Zw denote the internal resistance, charge transfer resistance, double-capacitance resistance and Warburg impedance of lithium ion diffusion, respectively.

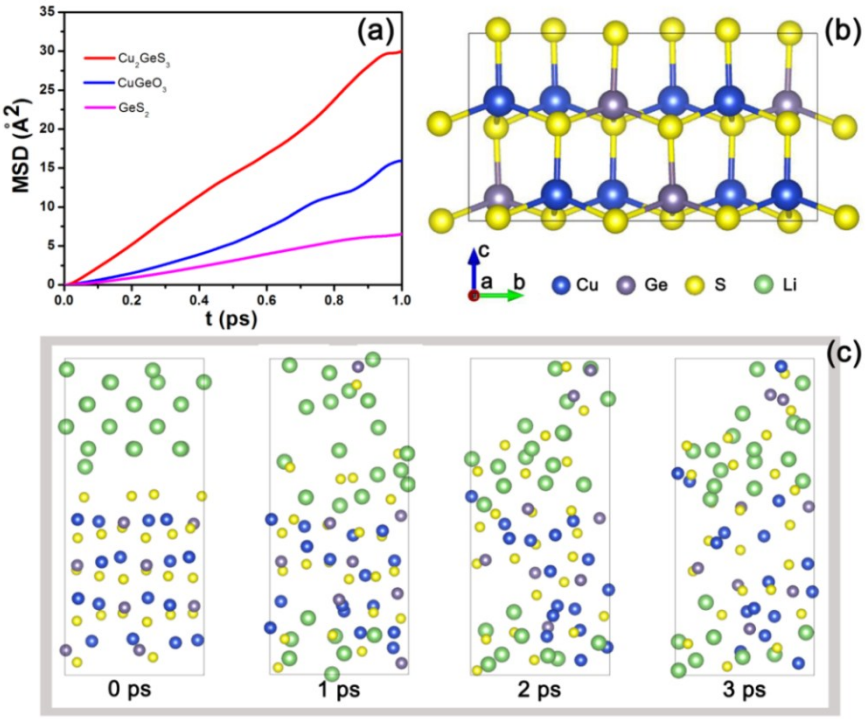

Fig. S10 (a) Total mean square displacement (MSD) of Li atoms. (b) Crystal structure of CGS. (c) Structural evolution of the CGS upon annealing at 700 K for 3 ps.

It is known that the diffusion coefficient (D) is obtained as the MSD over time:

$$D = \frac{1}{6t}\sum_{i}\left\langle [\mathbf{r}_i(t+t_0)]^2 - [\mathbf{r}_i(t_0)]^2 \right\rangle$$

Where $r_i(t)$ is the displacement of the i-th lithium ion at the time, and < > represents an average over the ensemble of atoms. It is evident from Fig. S10a, the diffusion coefficient of Li atoms is much more quickly in the CGS than that of $CuGeO_3$ and GeS_2. Structural relaxation of CGS were performed with generalized gradient approximation (GGA) in the projector augmented wave (PAW) method exchange-correlation functional, as implemented in the Vienna Ab initio Simulation Package (VASP).[9, 10] The plane-wave basis set was determined with a cutoff energy of 500 eV and the K-point mesh was defined such that the spacing of k-points became less than 0.25 Å for all calculations.[11] The crystal structure optimized was shown in the Fig.S10b. It was found that the the lattice of CGS was a= 6.519, b = 11.419 and c = 6.458 with Cc space group, consisting with the experimental results.[12] What's more, to elucidate the lithium ions diffusivity mechanism, the Ab initio Molecular Dynamic Simulations (AIMD) methods were performed. A final energy optimized was used to ensure the modeling in a local energy minimum, which was modeled by attaching an amorphous lithium atom layer of 24 atoms to the surface of a $1\times1\times2$ CGS supercell (49 atoms). Simulations were carried out using the NVT ensemble with the temperature controlled With a Nose thermostat at 700K for this modeling. Fig. S10c shows the structure evolution of the diffusion Li ions upon annealing at 700 K for 3 ps.

References

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