

## Supplementary Information

### Cobalt-doped Zn<sub>2</sub>GeO<sub>4</sub> Nanorods Assembled into Hollow Spheres as High-Performance Anode

#### Materials for Lithium-Ion Batteries

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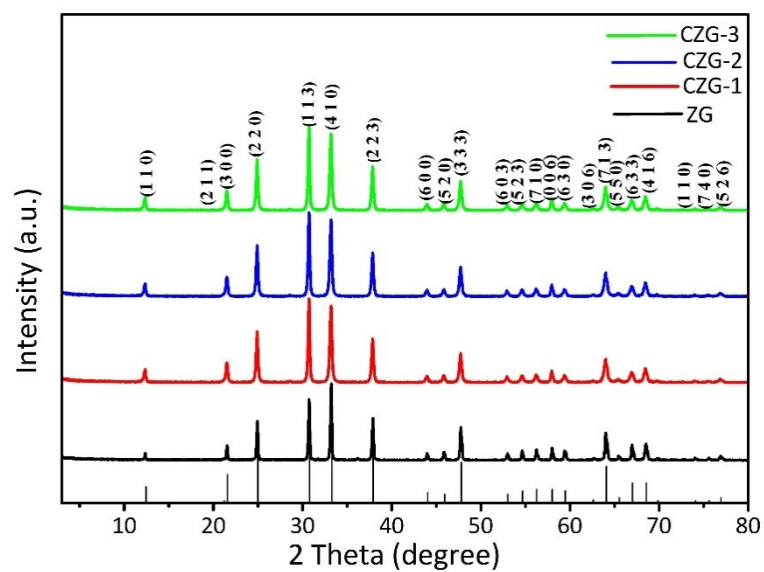
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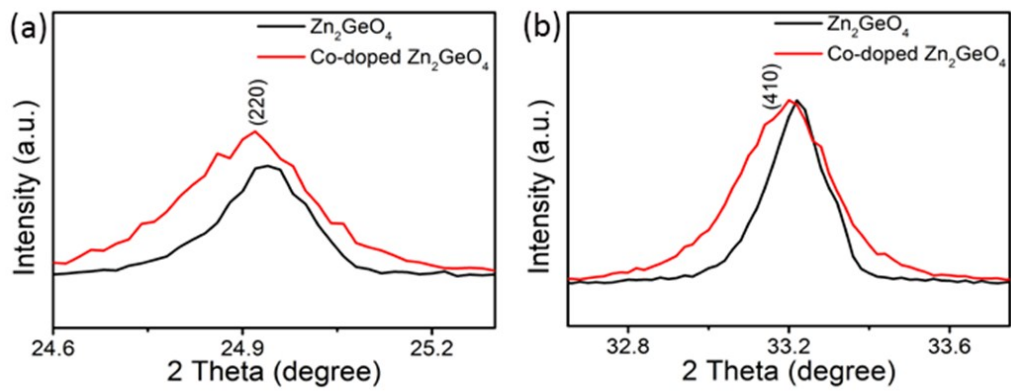
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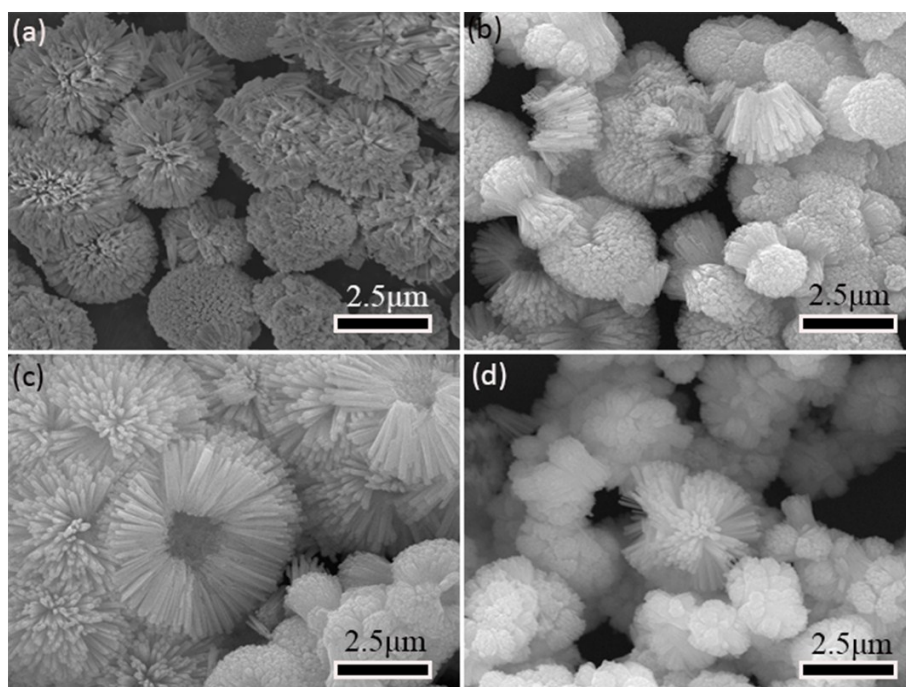
[+] These authors contributed equally to this work.



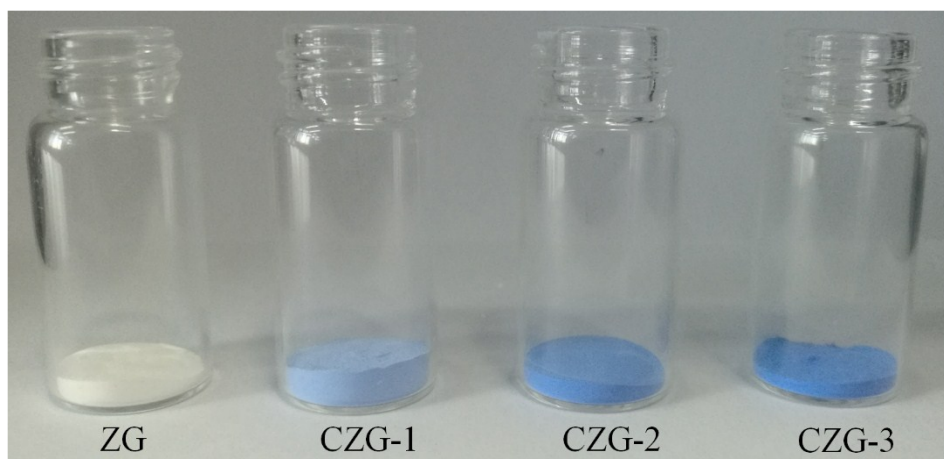
**Fig. S1** The XRD patterns of the as-prepared  $\text{Zn}_2\text{GeO}_4$  and Co-doped  $\text{Zn}_2\text{GeO}_4$  products.



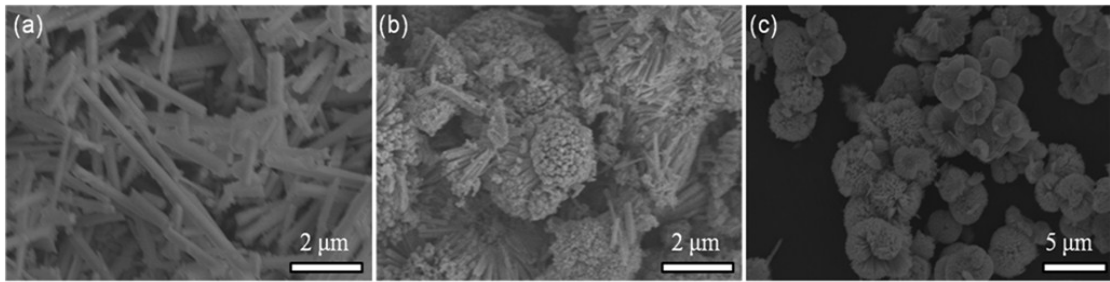
**Fig. S2** Magnified (220) and (410) peaks from the powder XRD date of pure  $Zn_2GeO_4$  and Co-doped  $Zn_2GeO_4$  samples.



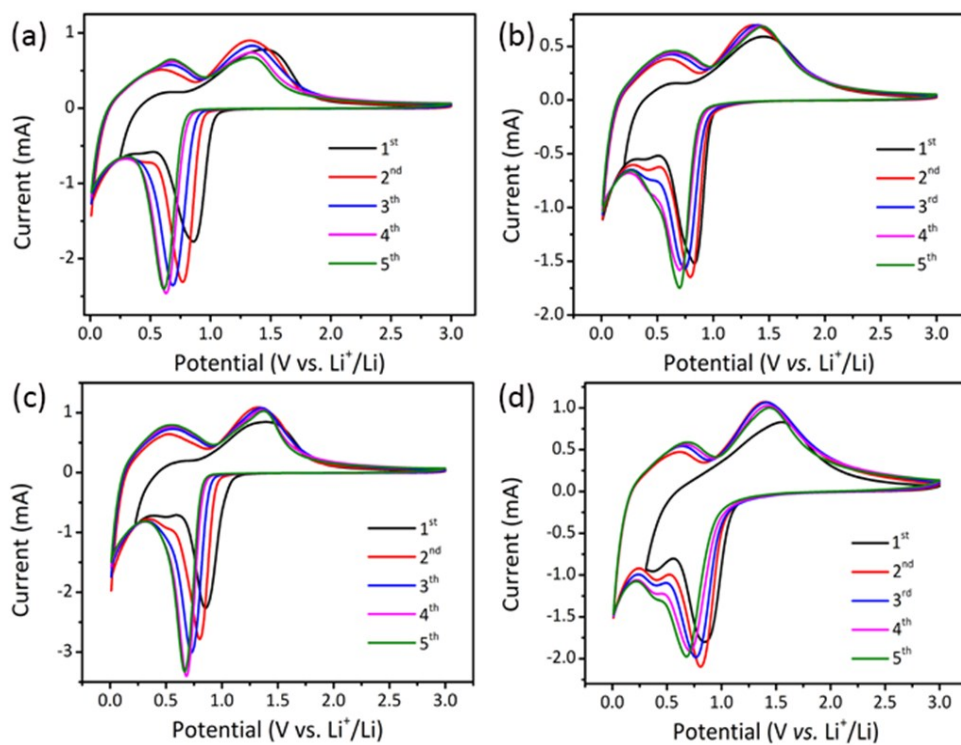
**Fig. S3** The FESEM images of ZG (a), CZG-1 (b), CZG-2 (c) and CZG-3 (d) hollow microspheres obtained.



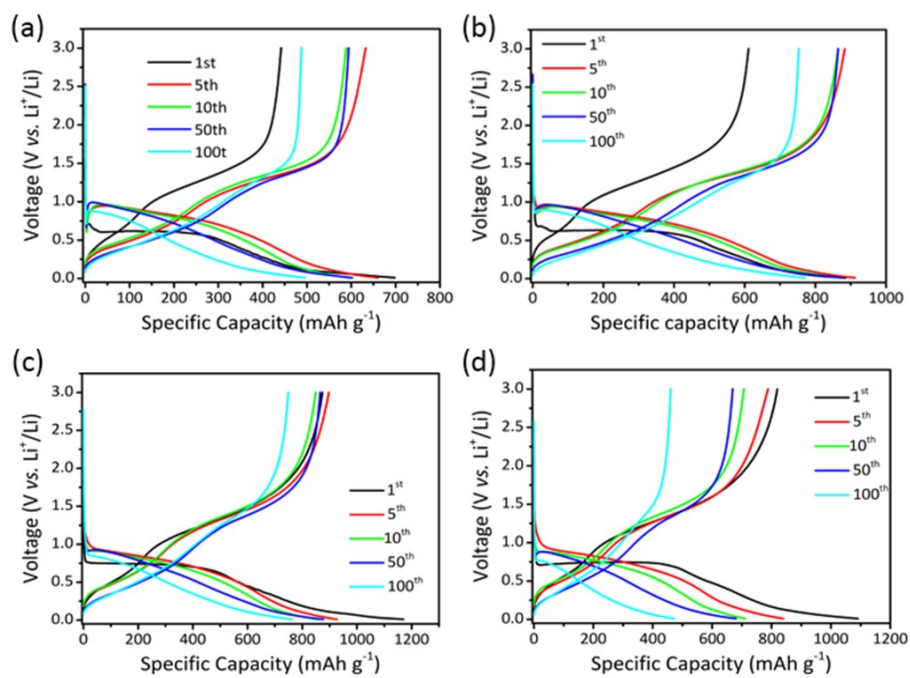
**Fig. S4** Color of the obtained products with different amount of Co doped, ZG (no Co doped), CZG-1 (5% Co doped), CZG-2 (10% Co doped) and CZG-3 (20% Co doped).



**Fig.S5** FESEM images of the products obtained with different amount of TEOA (a) 0 g, (b) 3.0 g, (c) 4.0 g.



**Fig. S6** The 1<sup>st</sup> five cycles of the cyclic voltamogram for ZG (a), CZG-1 (b), CZG-2 (c) and CZG-3 (d).



**Fig. S7** Galvanostatic charge-discharge profiles of ZG (a), CZG-1 (b), CZG-2 (c), CZG-3 (d) for selected cycles at a current density of  $1.0 \text{ A g}^{-1}$  with the potential window from 0.01 V to 3.0 V. The initial Coulombic Efficiency is 63%, 74%, 75%, 69% for ZG, CZG-1, CZG-2 and CZG-3, respectively.



**Table S1** Capacity retention after 100 charge/discharge cycles of the four samples with different Co<sup>2+</sup> doped concentration at a current density of 1.0 A g<sup>-1</sup>

Samples	Initial capacity/ mA h g <sup>-1</sup>	Capacity after 100 cycles/ mA h g <sup>-1</sup>	Capacity retention	Co <sup>2+</sup> concentration
ZG	698	496	71%	0
CZG-1	886	772	87%	5%
CZG-2	1419	882	62%	10%
CZG-3	1091	471	43%	20%

**Table S2** Comparison of the rate and cycling performance of Co-doped Zn<sub>2</sub>GeO<sub>4</sub> (CZG-2) in this work with those of bare Zn<sub>2</sub>GeO<sub>4</sub> and Zn<sub>2</sub>GeO<sub>4</sub>-based anodes materials with different morphology

Samples	Current density (mAh g <sup>-1</sup> )	Cycle number	Capacity (mAh g <sup>-1</sup> )	Ref.
Zn <sub>2</sub> GeO <sub>4</sub> with fascicular structure	500	160	1034	1
ZnO@amorphous Zn <sub>2</sub> GeO <sub>4</sub> core-shell hierarchical structure	500	250	905	2
Cobalt-doped Zn <sub>2</sub> GeO <sub>4</sub> nanorods assembled into hollow spheres	1000	100	882	This work
Zn <sub>2</sub> GeO <sub>4</sub> nanofibers anchored with amorphous carbon	2000	72	820	3
Zn <sub>2</sub> GeO <sub>4</sub> @carbon nanowires grown on Cu foils (with a 2 h reaction time)	2000	100	790	4

\*Some of the information was not specified in the literature and was estimated according to the data graphs.

## References

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- [3] H. H. Li, L. L. Zhang, C. Y. Fan, X. L. Wu, H. F. Wang, X. Y. Li, K. Wang, H. Z. Sun and J. P. Zhang, Flexible paper electrode constructed of Zn<sub>2</sub>GeO<sub>4</sub> nanofibers anchored with amorphous carbon for advanced lithium ion batteries, *J. Mater. Chem. A*, 2016, **4**, 2055-2059.
- [4] F. Zou, X. L. Hu, Y. M. Sun, W. Luo, F. F. Xia, L. Qie, Y. Jiang and Y. H. Huang, Microwave-induced in situ synthesis of Zn<sub>2</sub>GeO<sub>4</sub>/N-doped graphene nanocomposites and their lithium-storage properties, *Chem. Eur. J.*, 2013, **19**, 6027-6033.