Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

Germanium-Tin Alloy Nanocrystals for High-Performance Lithium Ion Batteries

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Table S1. Pressure of TMG and TMT vapors in the closed reactor, used to synthesize the NCs.

Sample No.	Composition of NC	Pressure of precursors (Torr)		Pressure ratio of TMT/(TMG+TMT)
		TMG	TMT	
1	Ge	40	0	0
2	$Ge_{0.95}Sn_{0.05}$	40	2	0.05
3	$Ge_{0.9}Sn_{0.1}$	50	5	0.1
4	$Ge_{0.75}Sn_{0.25}$-Sn	50	25	0.33
5	$Ge_{0.6}Sn_{0.4}$-Sn	25	25	0.5
6	$Ge_{0.6}Sn_{0.4}$-Sn	20	40	0.67
7	Sn	0	40	1

Fig. S1. The Sn content of NC products ([Sn]/([Ge]+[Sn]) vs. the partial pressure of Sn precursors (TMT) in gas phase ($p_{TMT}/(p_{TMG}+p_{TMT})$). The composition of $Ge_{1-x}Sn_x$–Sn composite (x = 0.1~0.4) was determined by XRD, EDX, and XPS. The x value of $Ge_{1-x}Sn_x$ alloy NC, which was solely determined using the XRD pattern, is also plotted (blue colored dots), showing that it increased linearly with the fraction of TMT in the gas mixture, but did not increase after 0.4.

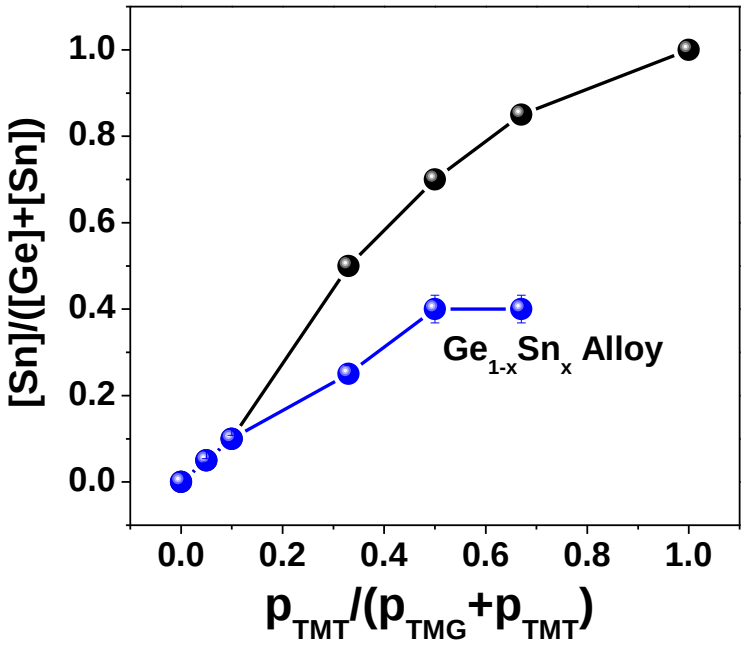
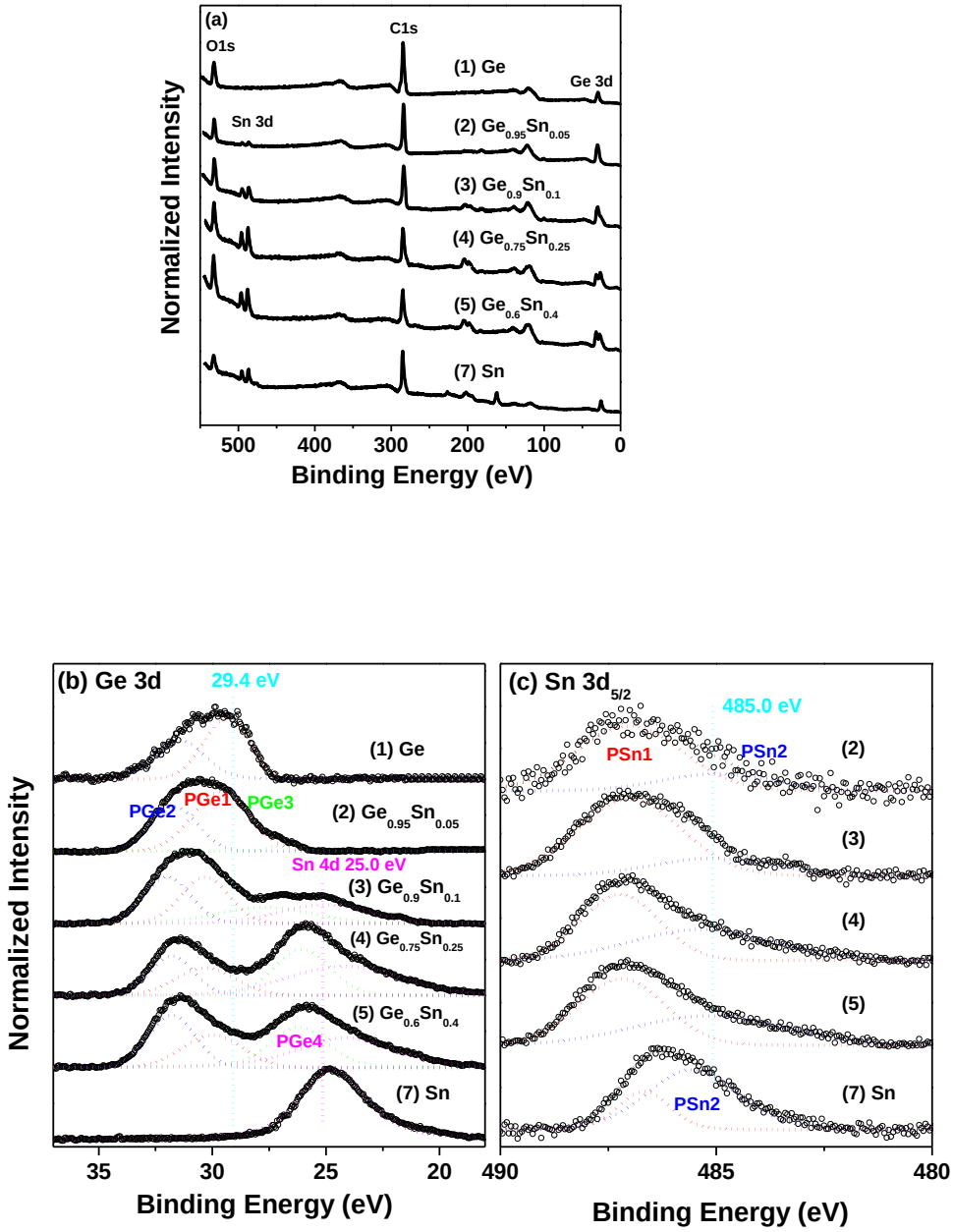


Fig. S2. (a) XPS survey scans, and fine-scanned (b) Ge 3*d* and (c) Sn $3d_{5/2}$ peaks of $Ge_{1-x}Sn_x$ NCs using a photon energy of 600 eV.



(a) Ge (1) and Sn (7) NC show the Ge and Sn peaks, respectively, and the C peak. The sample (2)~(5) showed the Ge, Sn, and C peaks, whose Sn peak intensity increases with *x*.

(b) The Ge (1) NC show an asymmetric peak centered at 29.7 eV, which is blue shifted from the bulk value (29.4 eV). The peak was able to resolve into two bands using the Voigt function, PGe1 (red dotted line) at 29.4 eV and PGe2 (blue dotted line) at 31.4 eV. The binding energy of the Ge atoms bonded to the C atoms is expected to appear at a higher compared to that of the Ge atoms bonded directly to the Ge atoms, based on the Pauling's electronegativity (χ_P) differences between Ge (χ_P = 2.01) and C (χ_P = 2.5). Therefore, the PGe1 and PGe2 bands are assigned to the Ge-Ge and Ge-C bonding structures, respectively. The Sn 4*d* peak of Sn (7) NC appears at ~ 25 eV, which is consistent with that of the bulk Sn metal.

The alloy NCs show a broader peak width than that of Ge. The peak of $Ge_{0.95}Sn_{0.05}$ was relsoved into the PGe1, PGe2, and PGe3 (green dotted line) bands at 29.6 eV, 31.3 eV, and 26.8 eV, respectively, which are assigned to the Ge-Ge, Ge-C, and Ge-Sn bonding structures. The χ_P of Sn (1.7) is lower than that of Ge, so the Ge-Sn bonding stucture is expected to have a lower binding energy than that of Ge-Ge. As the Sn composition increases, the Sn 4*d* peak appears partly overlapped with the Ge peak. Therefore, the peak of $Ge_{0.9}Sn_{0.1}$ was relsoved into the PGe1, PGe2, PGe3, and PGe4 (magenta dotted line) bands at 30.1 eV, 31.9 eV, 27.0, and 24.8 eV, respectively, which are assigned to the Ge-Ge, Ge-C, Ge-Sn, and Sn-Sn bonding structures. The peak of $Ge_{0.75}Sn_{0.25}$–Sn and $Ge_{0.6}Sn_{0.4}$–Sn was also resolved into four bonding structures. As *x* increases, the fraction of PGe1 band decreases, while that of PGe4 band increases due to the separated β-Sn phase. The peak area % and FWHM of the resolved bands are summarized in Table S2.

Table S2. Fitting parameters of Ge 3*d* peaks

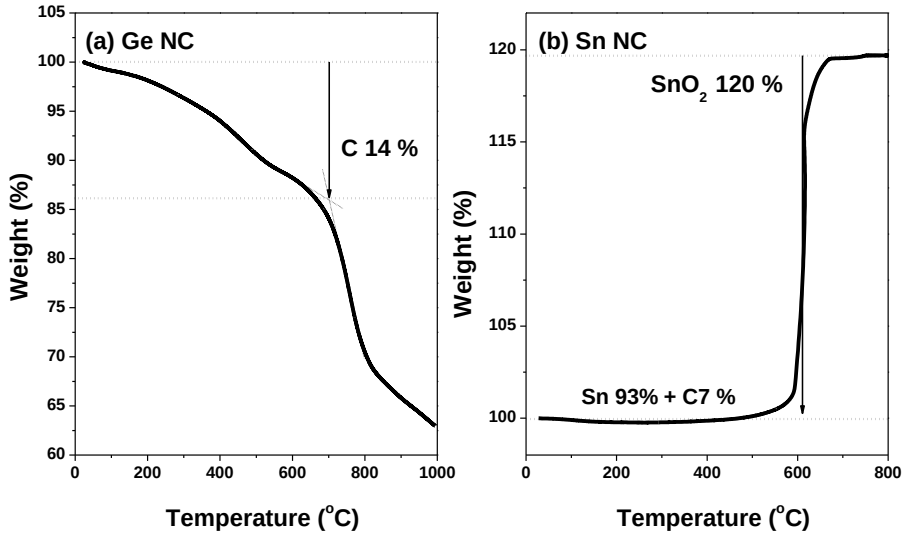
Sample	Peak	Position (eV)	FWHM (eV)	Area (%)
(1) Ge	PGe1	29.4	2.4	58
	PGe2	31.4	2.5	42
(2) $Ge_{0.95}Sn_{0.05}$	PGe1	29.6	2.9	60
	PGe2	32.0	2.4	37
	PGe3	26.8	1.4	3
(3) $Ge_{0.9}Sn_{0.1}$	PGe1	30.1	3.0	40
	PGe2	31.9	2.5	29
	PGe3	27.0	1.9	10
	PGe4	24.8	3.3	21
(4) $Ge_{0.75}Sn_{0.25}$	PGe1	30.3	3.1	18
	PGe2	32.0	2.2	19
	PGe3	26.1	2.9	28
	PGe4	24.2	5.9	35
(5) $Ge_{0.6}Sn_{0.4}$	PGe1	30.0	3.1	19
	PGe2	31.8	2.4	24
	PGe3	26.2	3.0	25
	PGe4	24.2	5.0	32
(7) Sn	PGe4	24.7	3.5	100

(c) The Sn $3d_{5/2}$ binding energy of Sn (7) NC is 486.2 eV, which is higher than that of the bulk Sn (485.0 eV), which is probably due to the bonding structures of the C outerlayers based on the Pauling's χ_P differences between Sn (χ_P = 1.7) and C (χ_P = 2.5). The peak was resolved by the PSn1 (red dotted line) band at 486.7 eV and the PSn2 (blue dotted line) band at 485.5 eV, corresponding to the Sn-C and Sn-Sn bonding structures, respectively. The $Ge_{1-x}Sn_x$ shows a significantly blue shifted peak centered at 487.2 eV, due to the Sn-Ge bonding structures. As *x* increases, the peak becomes more aymmetric at the lower energy side, due to the seprated β-Sn phase. The peak was resolved by the PSn1 band at 487.0~487.2 eV and the PSn2 band at 485.0~485.3 eV, corresponding to the Sn-Ge/Sn-C and Sn-Sn bonding structures, respectively. The peak area % and FWHM of the resolved bands are summarized in Table S3. The fraction of the Sn-Sn bonding structure (PSn2) increases with *x*, which is coherent with the XRD data. At *x* = 0.05 and 0.1, the fraction of PSn2 is very small, due to negligible separation of β-Sn phase.

Table S3. Fitting parameters of Sn $3d_{5/2}$ peak

Sample	Peak	Position (eV)	FWHM (eV)	Area (%)
(2) $Ge_{0.95}Sn_{0.05}$	PSn1	487.0	2.9	78
	PSn2	485.0	3.0	22
(3) $Ge_{0.9}Sn_{0.1}$	PSn1	487.0	2.8	80
	PSn2	485.1	3.2	20
(4) $Ge_{0.75}Sn_{0.25}$	PSn1	487.2	2.1	54
	PSn2	485.3	3.9	46
(5) $Ge_{0.6}Sn_{0.4}$	PSn1	487.2	2.4	57
	PSn2	485.2	4.1	43
(7) Sn	PSn1	486.7	1.4	27
	PSn2	485.5	2.1	73

Fig. S3. TGA analysis data of (a) Ge and (b) Sn NCs. In the case of Ge NC, the C oxidation (in air) to CO or CO_2 at 700 °C casuses the weight loss by 14%, corresponding to 14 wt.% C. The Sn NC underogoes simultaneously the Sn and C oxidation to gain the weight 120%. The oxidation of 100 g Sn to SnO_2 is expected to increase the weight by 127%. The weight increase of 120% implies that the C content 7 wt.% is lost. EDX data shows that average C content of (c) Ge and (d) Sn NC is about 50 atomic %, coresponding to 17 wt.%. Elemental analysis data provides that C = 17.6 wt.%, H = 1.6 wt.%. Therefore the C content is estimated to be avg. 15 wt.%.



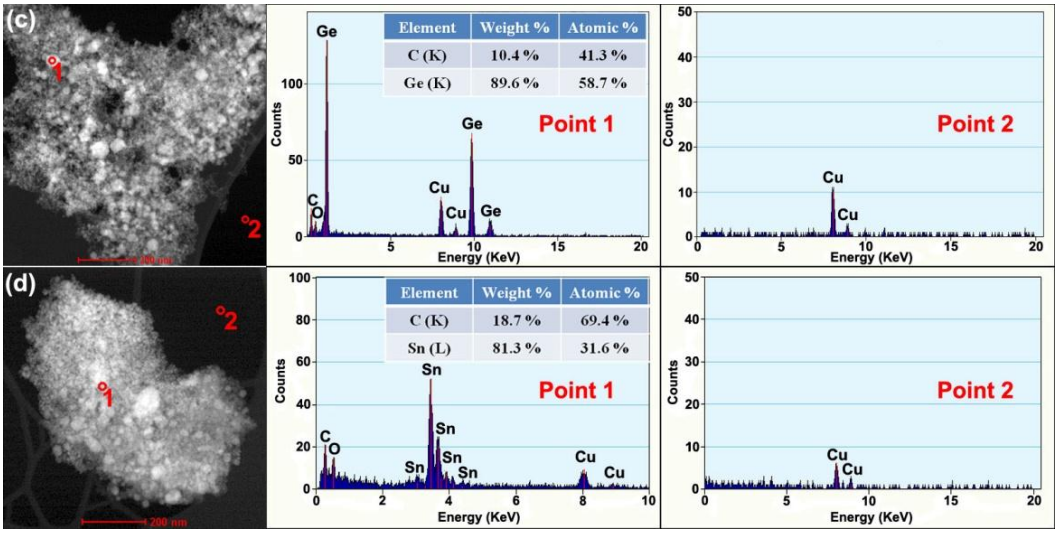


Fig. S4. Coulombic efficiency vs. cycle number for charge/discharge capacity of Ge (Ref. 15), $Ge_{0.95}Sn_{0.05}$, $Ge_{0.9}Sn_{0.1}$, and Sn NC with a rate of 0.1C.