

Supporting Information

Reversible Networked Porous Formation in Sb Nanoparticles during Cycles: Sb Nanoparticles Encapsulated into Nitrogen-Doped Carbon Matrix with Nanorods Structure for High-Performance Li-ion Batteries

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I. Experimental section

1.1 Synthesis of SbPO₄ nanorods

SbPO₄ nanorods as the sacrificial template were initially synthesized through a hydrothermal reaction. Typically, 0.228 g of SbCl₃, 0.345g of NH₄H₂PO₄ were dissolved into 40 ml of ethylene glycol at room temperature. This dispersion was heated to 70 °C and transferred to a Teflon-lined stainless autoclave at 160 °C for 4 h in an electric oven. After being cooled to room temperature naturally, the precipitate was collected and washed with deionized water and ethanol several times by centrifugation, then dried at 60 °C overnight to obtain SbPO₄ nanorods.

1.2 Synthesis of hollow Sb_2O_5 nanorods

To prepare Sb_2O_5 nanorods, 100 mg of the prepared SbPO_4 nanorods and 165mg KMnO_4 were added to 30 ml of deionized water under ultrasonication for 20 min. After the suspension was placed into a 100 ml flask and maintained at 75 °C for 12 h. After being cooled to room temperature naturally, the precipitate was collected and washed with deionized water and ethanol several times by centrifugation, then dried at 60 °C overnight to obtain hollow Sb_2O_5 nanorods.

1.3 Synthesis of Sb@N-MC nanorod

In a typical synthesis, 50 mg of Sb_2O_5 powder was dispersed in 50 ml Tris-buffer solution (10 mM, pH =8.5) and sonicated for 30 min. To coat a polydopamine shell, 50 mg of dopamine hydrochloride was added in the solution and stirred for 2 h. The resultant brownish black solution was washed with DI water and ethanol for several times and then dried under vacuum overnight. The obtained dark brown powder was put into a tube furnace and annealed at 500 °C under Ar/H_2 atmosphere for 4 h with a heating rate of 2 °C min. After being cooled to room temperature naturally, Sb@N-MC nanorod was obtained.

1.4 Synthesis Sb nanoparticles

Sb nanoparticles were synthesized by a wet chemical method. 0.45 g of NaBH_4 was dissolved in 13 mL of NMP in a three-necked flask under argon protection and heated to 60 °C. Subsequently, 0.68 g of SbCl_3 dissolved in 2 mL of NMP was immediately injected

via a syringe. The reaction mixture swiftly turned black and was cooled down quickly using an ice water bath. After cooling down to room temperature, the resultant Sb nanoparticles were collected by centrifugation, washed with deionized water several times, and dried at 40 °C overnight.

1.5 Synthesis SbNP@C nanoparticles

Synthesis of Sb@C nanoparticles. 0.1g Sb nanoparticles were dispersed in 75ml ethanol/water solution (v/v 1:2), and then 0.25g 3-aminophenol, 0.075g hexadecyl trimethyl ammonium Bromide, 0.25ml formaldehyde solution, were added to start the reaction with 0.1ml ammonia aqueous solution as catalyst. The reacting solution was stirred continuously at room temperature for 30 min. And then, the resultant Sb@RF nanoparticles were collected by centrifugation, washed with deionized water several times, and dried at 40 °C overnight. Finally, the obtained Sb@RF powder was put into a tube furnace and annealed at 500 °C under Ar/H₂ atmosphere for 4 h with a heating rate of 2 °C min. After being cooled to room temperature naturally, SbNP@C nanoparticles was obtained.

II. The thermogravimetric analysis of carbon content for Sb@N-CM nanorods

In order to ascertain carbon content for Sb-C composite materials, the thermogravimetric analysis (TGA) measurement has been conducted in air. As can be seen from Fig. 6, the slight weight loss for SbNP, Sb@N-CM nanorods, and SbNP@C is attributed to the adsorption of water below 300 °C. The weight gain of SbNP between 300~500 °C is due to the slightly oxidation of Sb to Sb₂O₃ ($4\text{Sb} + 3\text{O}_2 = 2\text{Sb}_2\text{O}_3$). However, the huge weight loss for Sb@N-CM nanorods, and SbNP@C is mainly attributed to the combustion of carbon to CO₂ and oxidation of Sb into Sb₂O₃. And then, the weight remains no change until 500 °C, indicating the entirely oxidation of the combustion of carbon to CO₂ and oxidation of Sb into Sb₂O₃ for different samples. Finally, the carbon content of Sb@N-CM nanorods, and SbNP@C sample is calculated to ~33 and ~59%, respectively.

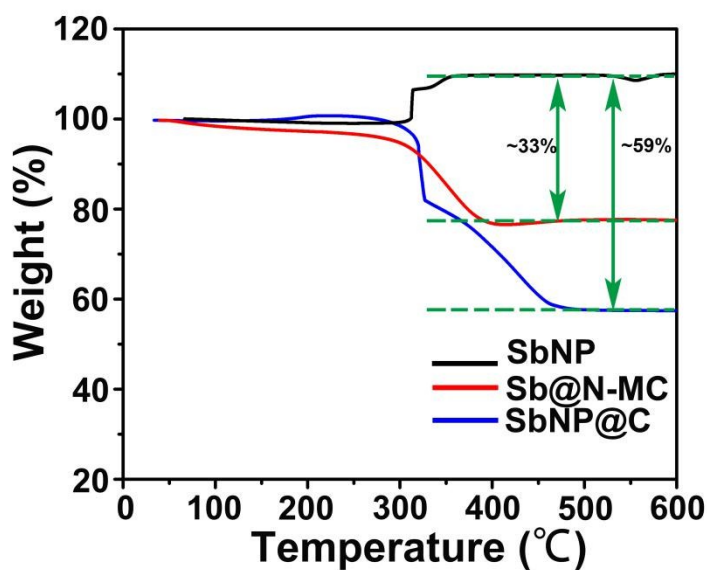


Fig. S1. TGA curves of SbNP, Sb@N-CM nanorods, and SbNP@C, respectively.

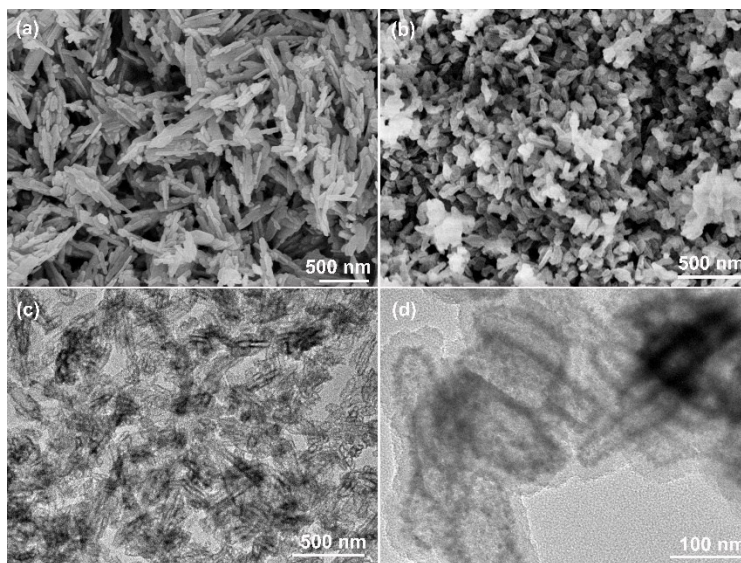


Fig. S2 (a) SEM image of SbPO_4 nanorods. (b, c) SEM and TEM image of porous Sb_2O_5 hollow nanorods. (d) TEM image of hollow $\text{PDA}@ \text{Sb}_2\text{O}_5 @ \text{PDA}$ nanorods.

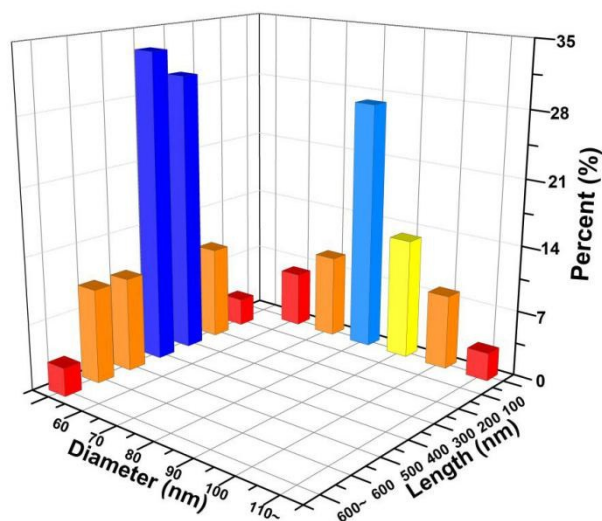


Fig. S3. The average diameter and length distribution of the $\text{Sb}@ \text{N-CM}$ nanorods.

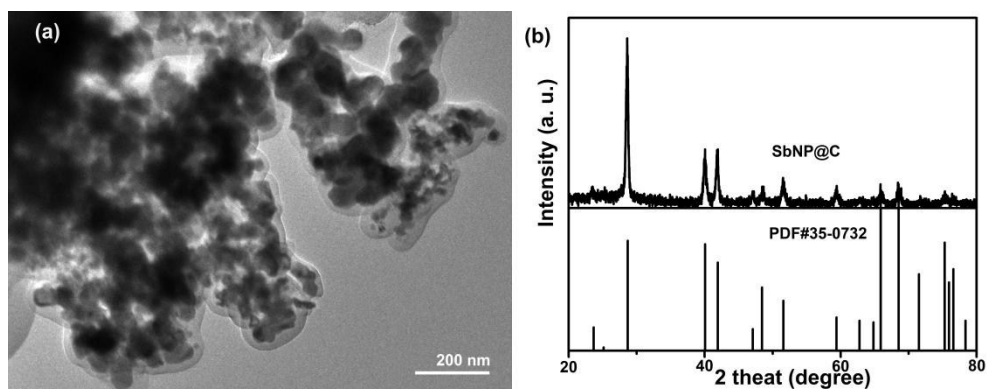


Fig. S4 (a) TEM image of the Sb@C nanoparticles. (b) XRD pattern of the Sb@C nanoparticles.

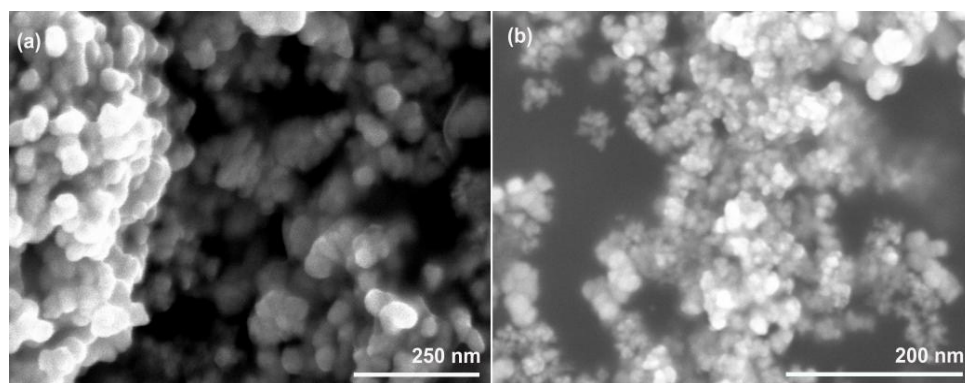


Fig. S5 (a, b) SEM images of the Sb nanoparticles.

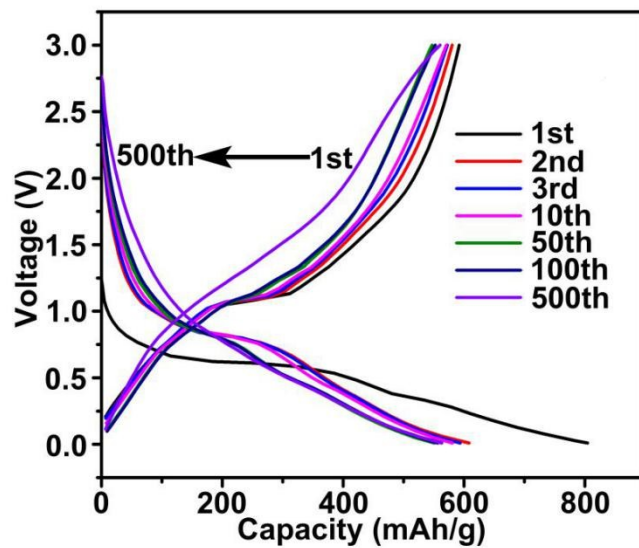


Fig. S6. The galvanostatic charge and discharge profiles of Sb@N-CM nanorods at a current density of 1000 mA g^{-1} for different cycles.

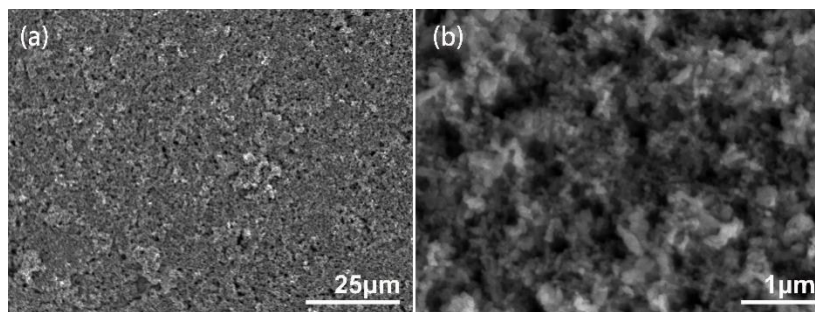


Fig. 7 (a, b) the SEM images of the Sb@N-CM nanorods electrode before cycle.

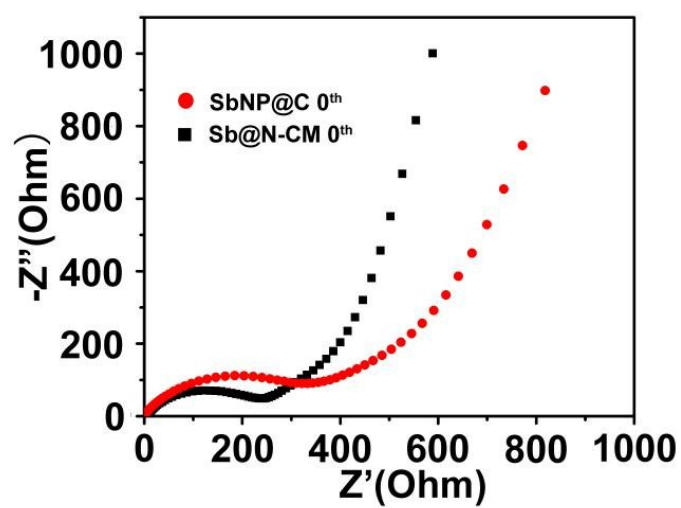


Fig. S8. The electrochemical impedance spectra of Sb@N-CM nanorods electrode and Sb@C nanoparticles electrode before cycles.

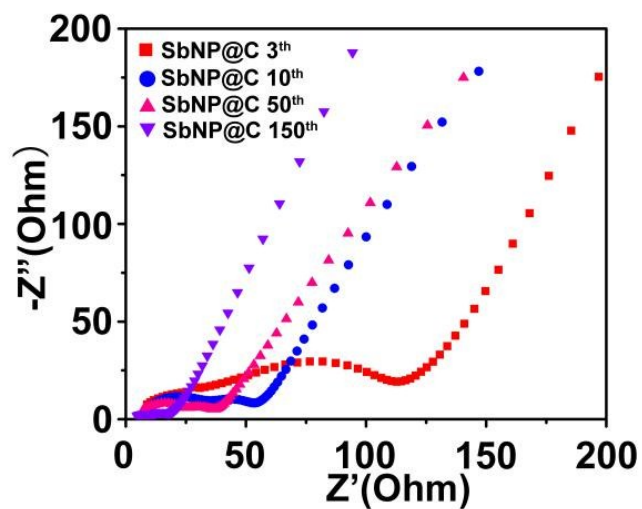


Fig. S9. The electrochemical impedance spectra of Sb@C nanoparticles electrode after different cycles.

Table S1. Comparison of the cycle performances of Sb@N-MC nanorod electrode with other Sb-based anode materials reported in the literature.

Electrodes	Current density (mA g ⁻¹)	Cycle number	Reversible capacity (mA h g ⁻¹)	Reversible capacity (mA h g ⁻¹)	capacity retention (%)	Ref.
Sb@N-MC nanorod	200	190	706.8	695.6	100.3	This work
	1000	500	593.5	591.8	99.7	
hollow Sb@C yolk-shell spheres	50	100	680	525	77.2	13
	1000	300		405		
Sb@TiO _{2-x} nanotubes	660	1000		547		20
	3300	1000		445		
	6600	1000		424		
Sb@N-C	200	300	650.8	602.8	92.7	21
	2000	3000	467.6	395	84.5	
monodisperse Sb nanocrystals	330	100	600			15
	2640	100				
antimony/amorphous carbon/graphene	500	400	665.4	592	88.9	19
	1000	700		413		
SiO ₂ /Sb@CNF	500	400		572		14
	1000	400		468		
C/Sb composites	100	200	595.5	466.2	78.3	25
G@NiSb/Sb@NF	200	50		340		18
ball milled Sb-carbon	230	250	612	550	89.8	29

Sb/NPC	200	100		556		30
rod-like Sb-C	100	100	687.1	478.8	69.7	31
Sb/graphene	100	40		411		32
	400	40		250		
RGO-SbTF-Ni	100	50	576.1	424.1	73.6	33
Sb/C composite	200	100	617	565	91.5	34
	1000	500		400.5		
Sb/carbon fiber	100	100	680	315.9	46.5	35

References

- 13 J. Liu, L. Yu, C. Wu, Y. Wen, K. Yin, F. K. Chiang, R. Hu, J. Liu, L. Sun, L. Gu, J. Maier, Y. Yu and M. Zhu, *Nano Lett.*, 2017, **17**, 2034-2042.
- 20 N. N. Wang, Z. C. Bai, Y. T. Qian and J. Yang, *Adv. Mater.*, 2016, **28**, 4126-4133.
- 21 W. Luo, F. Li, J. J. Gaumet, P. Magri, S. Diliberto, L. Zhou and L. Q. Mai, *Adv. Energy Mater.*, 2018, **8**, 1703237.
- 15 M. He, K. Kravchyk, M. Walter and M. V. Kovalenko, *Nano Lett.*, 2014, **14**, 1255-1262.
- 19 Z. Z. Wang, J. Qu, S. M. Hao, Y. J. Zhang, F. Q. Kong and Z. Z. Yu, *ChemElectroChem*, 2018, **5**, 2653-2659.
- 14 H. K. Wang, X. M. Yang, Q. Z. Wu, Q. B. Zhang, H. X. Chen, H. M. Jing, J. K. Wang, S. B. Mi, A. L. Rogach and C. M. Niu, *ACS Nano*, 2018, **12**, 3406-3416.
- 25 Y. Cheng, Z. Yi, C. L. Wang, L. D. Wang, Y. M. Wu and L. M. Wang, *Chem. Asian J.*, 2016, **11**, 2173-2180.

- 18 Y. L. Ding, C. Wu, P. Kopold, P. A. van Aken, J. Maier and Y. Yu, *Small*, 2015, **11**, 6026-6035.
- 29 T. Ramireddy, M. M. Rahman, T. Xing, Y. Chen and A. M. Glushenkov, *J. Mater. Chem. A*, 2014, **2**, 4282-4291.
- 30 Q. Yang, J. Zhou, G. Zhang, C. Guo, M. Li, Y. Zhu and Y. Qian, *J. Mater. Chem. A*, 2017, **5**, 12144-12148.
- 31 L. Fan, J. J. Zhang, J. H. Cui, Y. C. Zhu, J. W. Liang, L. L. Wan and Y. T. Qian, *J. Mater. Chem. A*, 2015, **3**, 3276-3280.
- 32 Y. D. Zhang, J. Xie, T. J. Zhu, G. S. Cao, X. B. Zhao and S. C. Zhang, *J. Power Sources*, 2014, **247**, 204-212.
- 33 Z. Yi, Q. G. Han, Y. Cheng, F. X. Wang, Y. M. Wu and L. M. Wang, *Electrochim. Acta*, 2016, **190**, 804-810.
- 34 Z. Yi, Q. Han, P. Zan, Y. Wu, Y. Cheng and L. Wang, *J. Power Sources*, 2016, **331**, 16-21.
- 35 H. Lv, S. Qiu, G. Lu, Y. Fu, X. Li, C. Hu and J. Liu, *Electrochim. Acta*, 2015, **151**, 214-221.