SUPPLEMENTARY INFORMATION

Sodium-ion storage performance of hierarchical-structured

(Co1/3Fe2/3)Se2 nanofibers with fiber-in-tube nanostructures

Young Jun Hong, Jung Hyun Kim and Yun Chan Kang*

Department of Materials Science and Engineering, Korea University, Anam-dong, Seongbuk-

gu, Seoul 136-713, Republic of Korea

E-mail: yckang@korea.ac.kr Fax: +82-2-928-3584; Tel: +82-2-3290-3268



Fig. S1 Morphologies of the electrospun fibers.



Fig. S2 XRD patterns of the CoFe₂O₄, $(Co_{1/3}Fe_{2/3})Se_2$, and $(Co_{1/3}Fe_{2/3})Se_2$ -Se-C composite nanofibers.



Fig. S3. EDAX spectrum and composition of the $(Co_{1/3}Fe_{2/3})Se_2$ nanofibers.



Fig. S4 XPS spectra of the hierarchical-structured (Co_{1/3}Fe_{2/3})Se₂ nanofibers: (a) survey scan,
(b) XPS spectrum of Co 2*p*, (c) XPS spectrum of Fe 2*p*, (c) XPS spectrum of Se 2*d*.



Fig. S5 The TG curves of the $(Co_{1/3}Fe_{2/3})Se_2$ -Se-C composite nanofibers measured under (a) Ar and (b) air atmospheres.



Fig. S6. N₂ adsorption and desorption isotherms and BJH pore size distributions of the $(Co_{1/3}Fe_{1/3})Se_2$ and $(Co_{1/3}Fe_{1/3})Se_2$ -Se-C nanofibers.



Fig. S7 The cycling performances of the hierarchical-structured ($Co_{1/3}Fe_{2/3}$)Se₂ nanofibers at a high current density of 5 A g⁻¹.



Fig. S8 The sodium-ion storage performances of the $CoFe_2O_4$ nanofibers with tube-in-tube structures: (a) cycling performances and (b) rate performances.



Fig. S9 SEM images of the (a) $(Co_{1/3}Fe_{2/3})Se_2$ and (b) $(Co_{1/3}Fe_{2/3})Se_2$ -Se-C sheets formed on glass substrate.

Table S1. Sodium-ion storage properties of various metal chalcogenides and Sb materials.

| metal chalcogenides & Sb materials | Synthesis | Electrochemical properties | Capacity retention | Ref |
|----------------------------------------------------------------|--------------------------------|------------------------------------------------------------------------|----------------------------------------------------------------|------|
| Cu ₃ P nanowire | In situ growth & phosphidation | 134 mA h g ⁻¹ after 260 cycles at 1.0 A g ⁻¹ | ~70 % | 3 |
| Tin phosphide | Ball milling | 718 mA h g ⁻¹ after 50 cycles at 0.1 A g ⁻¹ | - | 4 |
| Flower-like hierarchical Cu2NiSnS4 - rGO | Hydrothermal method | 321 mA h g ⁻¹ after 100 cycles at 0.05 A g ⁻¹ | - | 5 |
| Pyrite FeS ₂ | Hydrothermal method | ~200 mA h g ⁻¹ after 20,000 cycles at 1.0 A g ⁻¹ | ~90 % | 13 |
| | | ~170 mA h g ⁻¹ after 12,000 cycles at 20.0 A g^{-1} | - | |
| Vanadium sulfide on reduced graphene oxide layer | Hydrothermal method | ~241 mA h g ⁻¹ after 50 cycles at 0.1 A g ⁻¹ | - | 14 |
| Nickel disulphide graphene nanosheets composite | Hydrothermal method | 407 mA h g $^{-1}$ after 200 cycles at 0.087 A g $^{-1}$ | 77 % | 15 |
| MnS hollow microsphere | Hydrothermal method | 308 mA h g ⁻¹ after 125 cycles at 0.1 A g ⁻¹ | 62 % | - 16 |
| | | 118 mA h g ⁻¹ at 0.8 A g ⁻¹ | rate test | |
| Flower-like Sb ₂ S ₃ | Polyol reflux process | 641 mA h g ⁻¹ after 100 cycles at 0.2 A g ⁻¹ | 94 % (from the 50 th cycle) | 17 |
| | | 554.6 mA h g ⁻¹ at 2.0 A g ⁻¹ | rate test | |
| MoS ₂ /Graphene composite | Hydrothermal method | ~306 mA h g $^{\text{-1}}$ after 100 cycles at 0.02 A g $^{\text{-1}}$ | 61.3 % | 18 |
| FeSe ₂ microspheres | Hydrothermal method | 372 mA h g ⁻¹ after 2000 cycles at 1.0 A g ⁻¹ | 89 % | 19 |
| SnSe/carbon nanocomposite | Ball milling | 325 mA h g ⁻¹ after 200 cycles at 0.5 A g ⁻¹ | 72.5 % | 22 |
| SnSe alloy | Ball milling | 707 mA h g ⁻¹ after 50 cycles at 0.143 A g ⁻¹ | - | - 23 |
| | | ~350 mA h g ⁻¹ at 0.77 A g ⁻¹ | rate test | |
| MoSe ₂ yolk-shell microsphere | Spray pyrolysis | 433 mA h g $^{\text{-1}}$ after 50 cycles at 0.2 A g $^{\text{-1}}$ | 99 % (from the 2^{nd} cycle) | 24 |
| SnSe nanoplate | Spray pyrolysis | 558 mA h g ⁻¹ after 50 cycles at 0.3 A g ⁻¹ | 100 % (from the 2 nd cycle) | 25 |
| | | ~221 mA h g ⁻¹ at 2.0 A g ⁻¹ | rate test | |
| NiSe ₂ -rGO-C composite nanofiber | Electrospinning | 468 mA h g $^{\text{-1}}$ after 100 cycles at 0.2 A g $^{\text{-1}}$ | - | 26 |
| Graphitic carbon-coated FeSe ₂ | Electrospinning | 412 mA h g ⁻¹ after 150 cycles at 1.0 A g ⁻¹ | 82 % (from the 2^{nd} cycle) | 27 |
| Ultrathin MoS ₂ embedded in the carbon nanofiber | Electrospinning | 484 mA h g ⁻¹ after 100 cycles at 1.0 A g ⁻¹ | | 28 |
| | | 253 mA h g ⁻¹ after 100 cycles at 10.0 A g ⁻¹ | - | |
| CoSe _x -rGO composite | Spray pyrolysis | 420 mA h g ⁻¹ after 50 cycles at 0.3 A g ⁻¹ | $\frac{80 \%}{(\text{from the } 2^{\text{nd}} \text{ cycle})}$ | 29 |
| Nanoporous-Sb | Melt-spun | 574 mA h g ⁻¹ after 200 cycles at 0.1 A g ⁻¹ | - | 48 |

| Highly ordered Sb nanorod array | Nanoimprinted AAO templating technique | 521 mA h g $^{-1}$ after 250 cycles at 0.2 A g $^{-1}$ | ~84 % | 49 |
|--------------------------------------------------------------------------------------------|----------------------------------------------|------------------------------------------------------------------------|-----------------------------------------------------------------|---------------|
| Porous hollow Sb microspheres | Replacement reaction | 617 mA h g ⁻¹ after 100 cycles at 0.1 A g ⁻¹ | 97 % | - 50 |
| | | 313 mA h g ⁻¹ at 3.2 A g ⁻¹ | rate test | |
| Sb/C fibers | Electrospinning | 350 mA h g ⁻¹ after 300 cycles at 0.1 A g ⁻¹ | 83 % | 51 |
| Sb–C nanofibers | Electrospinning | 450 mA h g ⁻¹ after 400 cycles at 0.1 A g ⁻¹ | > 90 % | 52 |
| Monodisperse Sb nanocrystals | Colloidal synthesis | 580 mA h g ⁻¹ after 100 cycles at 0.66 A g ⁻¹ | > 90 % | 53 |
| Sb/MWCNT nanocomposite | Wet milled synthesis | 387 mA h g $^{\text{-1}}$ after 120 cycles at 0.2 A g $^{\text{-1}}$ | 76 % | 54 |
| rGO/nano Sb composite | Reduction method | 598 mA h g $^{-1}$ after 50 cycles at 0.131 A g $^{-1}$ | 93 % | - 55 |
| | | 100 mA h g ⁻¹ at 6.6 A g ⁻¹ | rate test | |
| Antimony/multilayer graphene hybrid | Confined vapor deposition method | 405 mA h g $^{\text{-1}}$ after 200 cycles at 0.1 A g $^{\text{-1}}$ | 90 % | 56 |
| Antimony hollow nanospheres | Galvanic replacementt | 622.2 mA h g $^{\text{-1}}$ after 50 cycles at 0.05 A g $^{\text{-1}}$ | - | - 57 |
| | | 315 mA h g ⁻¹ at 1.6 A g ⁻¹ | rate test | |
| Sb@C coaxial nanotubes | Thermal-reduction strategy | 407 mA h g ⁻¹ after 240 cycles at 0.1 A g ⁻¹ | - | - 58 |
| | | 240 mA h g $^{\text{-1}}$ after 2000 cycles at 1.0 A g $^{\text{-1}}$ | - | |
| Ultrafine Sb nanocrystals embedded in carbon microspheres | One-pot spray pyrolysis | 372 mA h g ⁻¹ after 100 cycles at 0.3 A g ⁻¹ | 90 % (from the 2 nd cycle) | 59 |
| Hierarchical-structured (Co _{1/3} Fe _{2/3})Se ₂ nanofiber | Electrospinning | 512 mA h g ⁻¹ after 60 cycles at 0.3 A g ⁻¹ | $\frac{100 \%}{(\text{from the } 2^{\text{nd}} \text{ cycle})}$ | This study |
| | | 441 mA h g ⁻¹ after 100 cycles at 5.0 A g ⁻¹ | 96 % (from the 2 nd cycle) | |