Supporting information

Compositionally tuned hybridization of n-type Ag⁰:Ag₂Se at ambient conditions towards excellent thermoelectric properties at room temperature

Author Si Yin Tee,* Daniel Ponsford, Xian Yi Tan, Xiaobai Wang, Chee Leng Lay, Coryl Jing Jun Lee, Xi Ping Ni, Debbie Hwee Leng Seng, Warintorn Thitsartarn, Guijian Guan, and Ming-Yong Han*



Fig. S1. SEM EDX spectra of the as-synthesized Ag⁰:Ag₂Se powders obtained after reaction for 2, 24, 48, 72, 120, and 168 h (denoted as Day 0-, 1-, 2-, 3-, 5-, and 7-day in the figure), possessing the molar ratios of Ag/Se of 4.07, 3.69, 2.38, 2.13, 2.09, and 2.04, respectively.



Fig. S2. (A) SEM and TEM (inset) images of the as-synthesized 1.96% Ag⁰:Ag₂Se powder at room temperature after 7 days of reaction. (B) Differential scanning calorimetry (DSC) thermogram of 1.96% Ag⁰:Ag₂Se powder.



Fig. S3. XRD patterns of the as-synthesized 1.96% Ag⁰:Ag₂Se powder (after 7 days of reaction), cold-pressed pellet (RT, 303 K), cold-pressed/annealed pellet (200 °C), and hot-pressed pellet (SPS at 200 °C).



Fig. S4. SEM images of 1.96% Ag⁰:Ag₂Se pellet after (A) cold-pressed/annealed at 200 °C and (B) hot-pressed at 200 °C by SPS.



Fig. S5. Thermoelectric performance of 1.96% $Ag^0:Ag_2Se$ pellet for 5 cycles (A) temperaturedependent σ and (B) temperature-dependent *S*.



Fig. S6. (A) SEM image, (B) EDX spectrum and (C) XRD pattern of the as-synthesized 93.81% Ag⁰:Ag₂Se nanoparticles for 2 min of reaction of NaBH₄ with AgNO₃ in the presence of HSe⁻.
(D) Optical images of the as-synthesized 93.81% Ag⁰:Ag₂Se after 2 min of reaction, and upon exposure of freshly formed Ag⁰ nanoparticles to air for a few minutes.



Fig. S7. Optical images of the as-synthesized Ag⁰:Ag₂Se after reaction at room temperature for 0, 1, 2, 3, 5, and 7 days, corresponding to excessive Ag⁰ at 50.86%, 45.80%, 15.97%, 6.10%, 4.31%, and 1.96%, respectively. Inset is the colourless solution of Na₂Se after chemical reduction of Na₂SeO₃ by NaBH₄.



Fig. S8. Ag 3d XPS spectra of the as-synthesized Ag⁰:Ag₂Se powders with excessive Ag⁰ at 93.81%, 6.10%, 4.31%, and 1.96% after reaction for 2 min, 3 days, 5 days, and 7 days, respectively.

Materials	Figure of merit (ZT)	Synthesis method	Ref.
Ag ₂ Se			
Ag ₂ Se	0.6 (300 K)	Hydrothermal	1
Ag ₂ Se	0.13 (300 K)	Colloidal synthesis	2
Ag ₂ Se	0.45 (323 K)	Chemical synthesis	3
Ag ₂ Se	0.55 (300 K)	Colloidal synthesis	4
Ag ₂ Se	0.7 (317 K)	Solvothermal	5
Ag ₂ Se	0.514 (300 K)	Chemical synthesis	6
Ag ₂ Se hybridized with other in	organic components		
1.96% Ag ⁰ :Ag ₂ Se	0.89 (303 K)	Chemical synthesis	Our work
(Cu2Se)0.05/(Ag2Se)0.95	0.15 (300 K) 0.45 (875 K)	Microwave-assisted thermolysis	7
Ag ₂ Se/Ag/CuAgS/nylon	0.5 (300 K)	Chemical synthesis	8
Ag ₂ Se/MWCNTs	0.05 (300 K)	Solvothermal	9
Ag ₂ Se/MWCNTs	0 19 (200 V)	Salvatharmal	10
	0.16 (SUU K)	Solvotherman	10
Ag ₂ Se/RGO	0.39 (363 K)	Hydrothermal	11

Table S1. Literature comparison between our work with bulk Ag_2Se and hybridized Ag_2Se

MWCNTs: multiwalled carbon nanotubes, RGO: reduced graphene oxide

References

- H. Wang, W. Chu, D. Wang, W. Mao, W. Pan, Y. Guo, Y. Xiong and H. Jin, Low-Temperature Thermoelectric Properties of β-Ag₂Se Synthesized by Hydrothermal Reaction, *J. Electron. Mater.*, 2011, 40, 624-628.
- 2. C. Xiao, J. Xu, K. Li, J. Feng, J. Yang and Y. Xie, Superionic phase transition in silver chalcogenide nanocrystals realizing optimized thermoelectric performance, *J. Am. Chem. Soc.*, 2012, **134**, 4287-4293.
- 3. C. Han, Z. Li, G. Q. Lu and S. Xue Dou, Robust scalable synthesis of surfactant-free thermoelectric metal chalcogenide nanostructures, *Nano Energy*, 2015, **15**, 193-204.
- 4. K. H. Lim, K. W. Wong, Y. Liu, Y. Zhang, D. Cadavid, A. Cabot and K. M. Ng, Critical role of nanoinclusions in silver selenide nanocomposites as a promising room temperature thermoelectric material, *J. Mater. Chem. C*, 2019, **7**, 2646-2652.
- 5. D. Li, J. H. Zhang, J. M. Li, J. Zhang and X. Y. Qin, High thermoelectric performance for an Ag₂Se-based material prepared by a wet chemical method, *Mater. Chem. Front.*, 2020, **4**, 875-880.
- 6. D. Lee, W. Park, Y. A. Kang, H. T. Lim, S. Park, Y. Mun, J. Kim and K. S. Jang, Substrate-Free Thermoelectric 25 um-Thick Ag₂Se Films with High Flexibility and In-Plane zT of 0.5 at Room Temperature, *ACS Appl. Mater. Interfaces*, 2023, **15**, 3047-3053.
- S. Ballikaya, Y. Oner, T. Temel, B. Ozkal, T. P. Bailey, M. S. Toprak and C. Uher, Thermoelectric and thermal stability improvements in Nano-Cu₂Se included Ag₂Se, *J. Solid State Chem.*, 2019, 273, 122-127.
- 8. Y. Lu, Y. Qiu, K. Cai, Y. Ding, M. Wang, C. Jiang, Q. Yao, C. Huang, L. Chen and J. He, Ultrahigh power factor and flexible silver selenide-based composite film for thermoelectric devices, *Energy Environ. Sci.*, 2020, **13**, 1240-1249.
- 9. N. Chen, C. Ren, L. Sun, H. Xue, H. Yang, X. An, X. Yang, J. Zhang and P. Che, Improved thermoelectric properties of multi-walled carbon nanotubes/Ag₂Se via controlling the composite ratio, *CrystEngComm*, 2022, **24**, 260-268.
- 10. D. Park, M. Kim and J. Kim, Preparation and structure dependent thermoelectric properties of flexible N-type nanostructured silver(I) selenide/multi-walled carbon nanotube composite film, *Appl. Surf. Sci.*, 2023, **613**.
- 11. R. Santhosh, R. Abinaya, J. Archana, S. Ponnusamy, S. Harish and M. Navaneethan, Controlled grain boundary interfaces of reduced graphene oxide in Ag₂Se matrix for low lattice thermal conductivity and enhanced power factor for thermoelectric applications, *J. Power Sources*, 2022, **525**.
- 12. A. S. Kshirsagar, C. Hiragond, A. Dey, P. V. More and P. K. Khanna, Band Engineered I/III/V–VI Binary Metal Selenide/MWCNT/PANI Nanocomposites for Potential Room Temperature Thermoelectric Applications, *ACS Appl. Energy Mater.*, 2019, **2**, 2680-2691.