Supporting Information

An alternative, faster and simpler method for the formation of hierarchically porous ZnO particles and their thermoelectric performance

Raymond V.Rivera Virtudazo,[a] Quansheng Guo,[a] Rudder Wu,[a] Toshiaki Takei,[b] and Takao Mori*[a]

[a]*Thermal Energy Materials Group, WPI Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044 Japan*

[b]*RNFS/Nanofabrication Group, WPI Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044 Japan*
**corresponding author. TEL: +81-(0)29-860-4323 FAX: +81-(0)29-860-6280*
**E-mail: MORI.Takao@nims.go.jp*

ABBREVIATIONS

ZT, Figure of Merit; XRD, X-ray Diffraction; SPS, Spark Plasma Sintering; DSC, Differential Scanning Calorimetry; Cp, Heat Capacity; SEM, Scanning Electron Microscope; EDX, Energy Dispersive X-ray; RE, Rare Earth

Keywords:
Energy conversion; Materials science; Semiconductors; Thermoelectric materials

Typical reaction of ZnO:

$6NH_4HCO_3 + 6H_2O \longrightarrow 6NH_4OH + 6H_2CO_3$ -----1

$5Zn(NO_3)_2 \longrightarrow 5Zn^{2+} + 10NO_3^-$ ----------2

(1)+ (2) ideal case

$5Zn^{2+}{}_{(aqs)} + 10NO_3^- + 6NH_4^+ + 12H^+ + 6CO_3^{2-} \longrightarrow$

$Zn_5(CO_3)_2(OH)_{6(s)} + 6NH_4^+ + 4H^+ + 10\,NO_3^- + 4H_2CO_3 + H_2O_{(aqs)} + CO_2$

$Zn_5(CO_3)_2(OH)_6 \longrightarrow 5ZnO + 2CO_2 + 3H_2O$ (annealing)

Fig.S1 Typical reaction for ZnO.

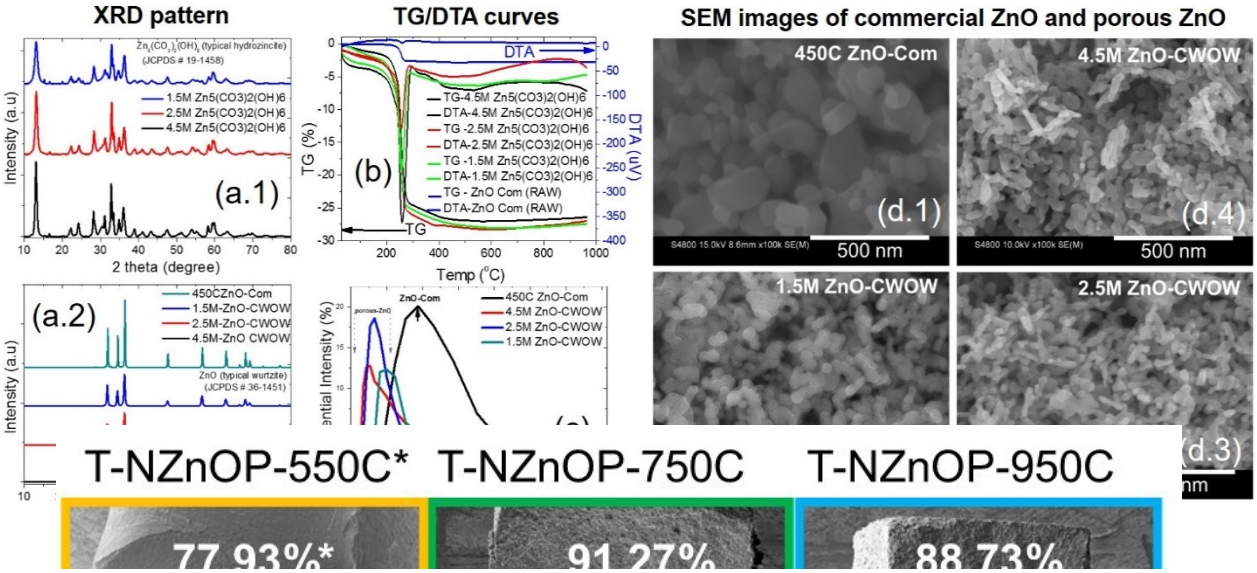


Fig.S2 (a) XRD pattern of (a.1) $Zn_5(CO_3)_2(OH)_6$ and (a.2) NZnO powder (b) TG/DTA curves of as synthesized $Zn_5(CO_3)_2(OH)_6$, (c) PSD curves and (d) SEM images at different concentration with commercial ZnO powder (as reference).

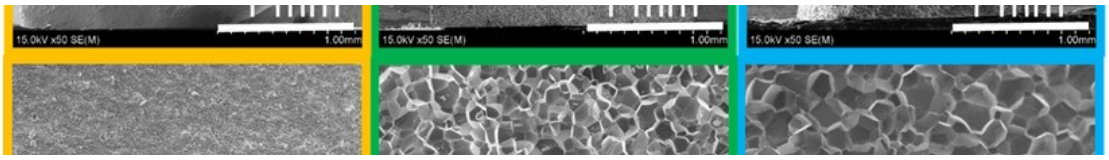
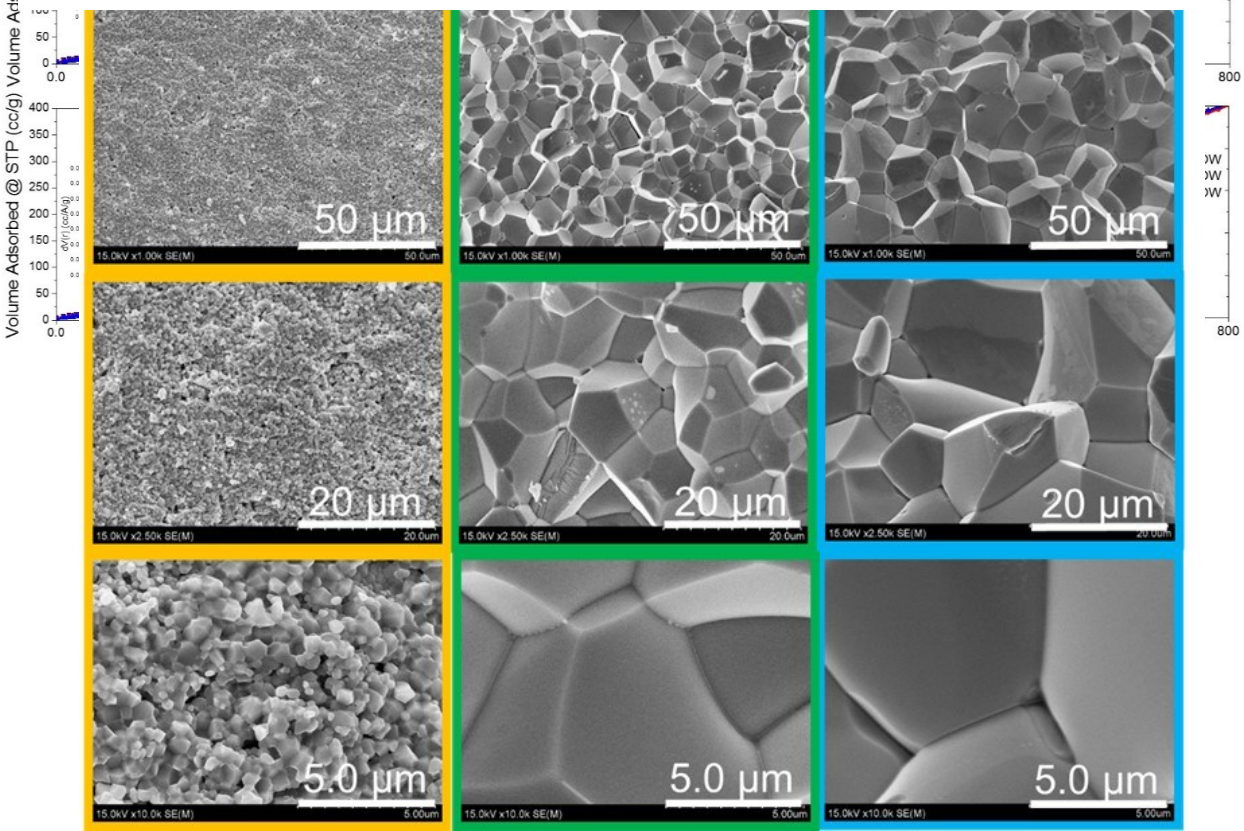


Fig.S3 (a) N_2 adsorption-desorption isotherm with pore-size distribution calculated by Barrett-Joyner-Halenda (BJH) method and density functional theory (DFT. inset) model of (a.1) $Zn_5(CO_3)_2(OH)_6$ and (a.2) NZnO powder; (b) Physicochemical properties of $Zn_5(CO_3)_2(OH)_6$ and NZnO powder with reference CZnO-Com (c) UV-Vis spectra of (c.1) $Zn_5(CO_3)_2(OH)_6$ and (c.2) NZnO powder with varying concentrations.



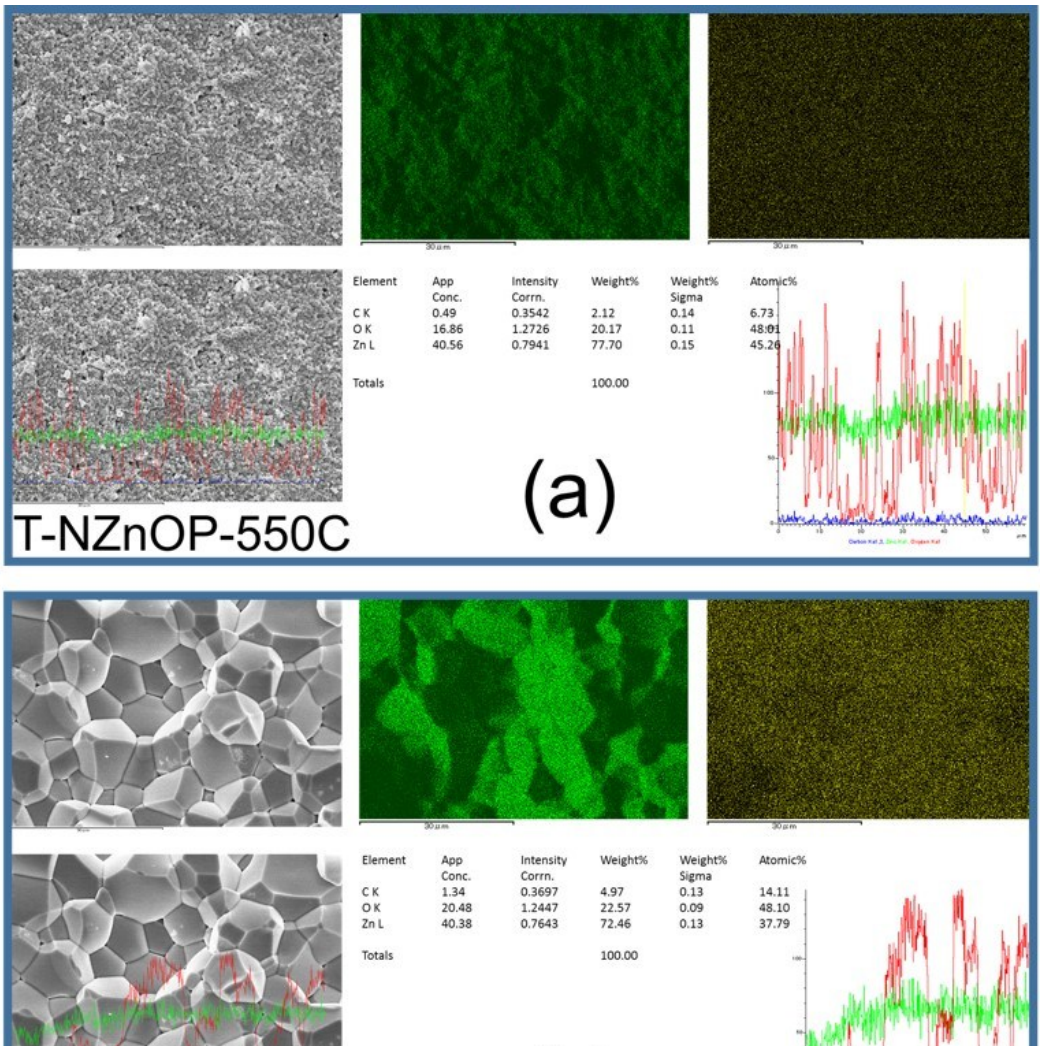


Fig.S4 Typical cross sectional area of sample pellets cut perpendicular to the applied pressure direction of low pressure spark plasma sintering (SPS) (2.2~2.8KN), for determining the thermoelectric properties.

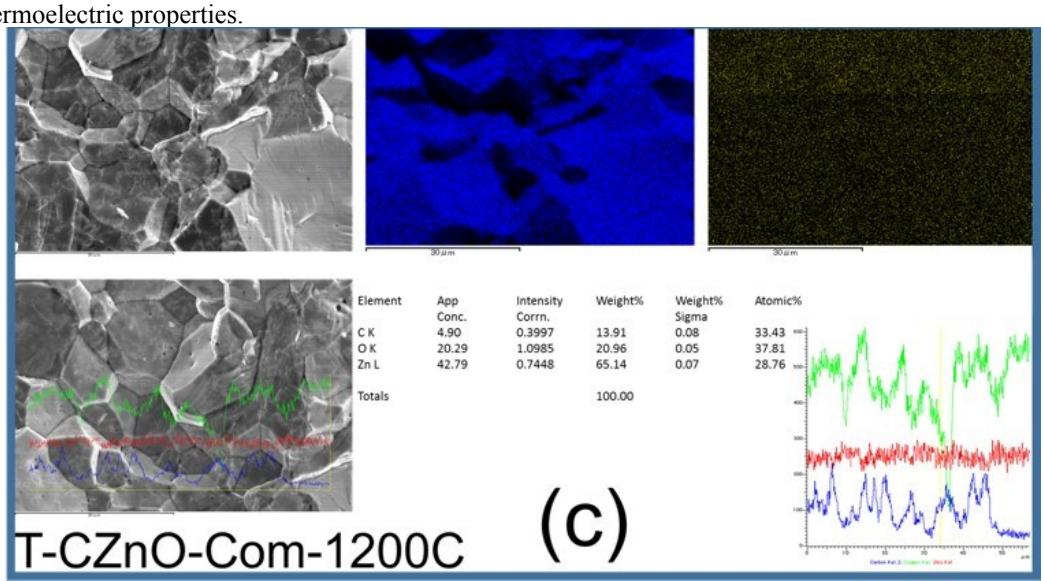


Fig.S5 Typical EDX analysis of (a,b) T-NZnOP series at varying sintering temperature with (c) T-CZnO-Com-1200C as reference.

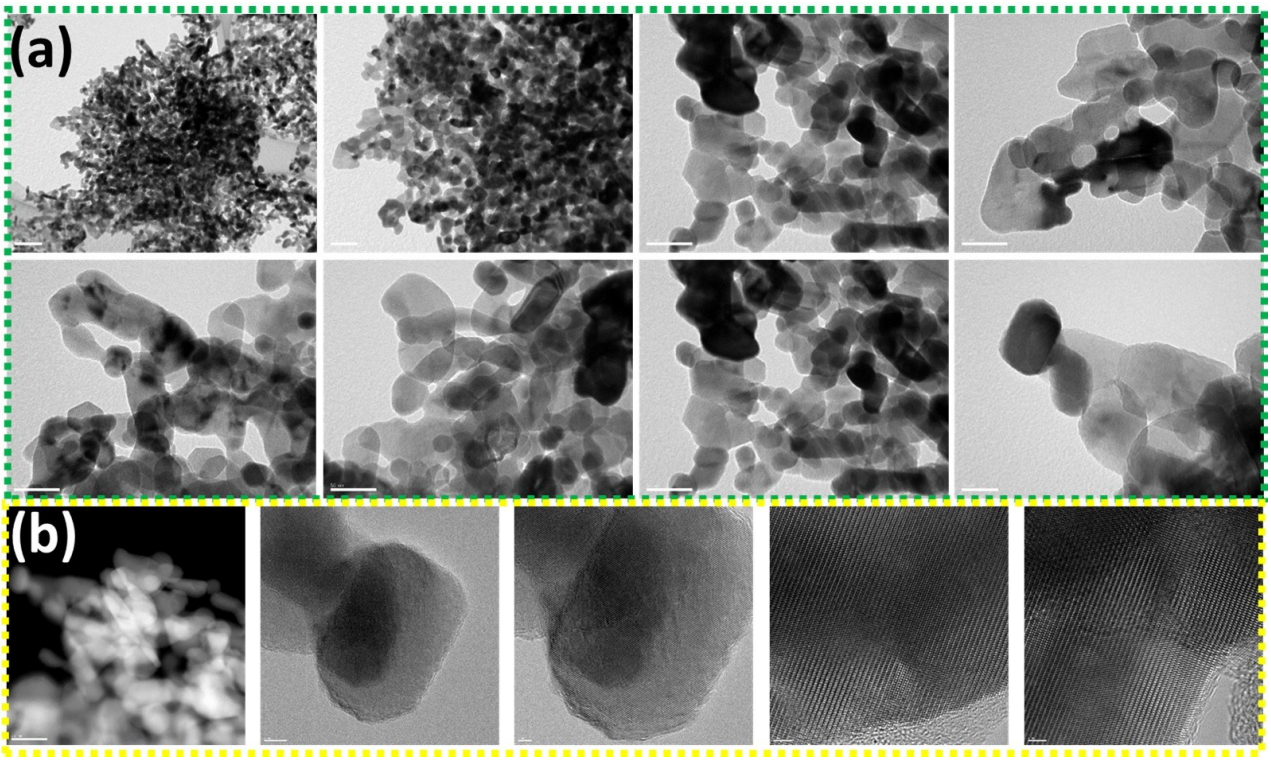


Fig.S6 (a) Series of TEM micrographs and (b) series of HR-TEM.

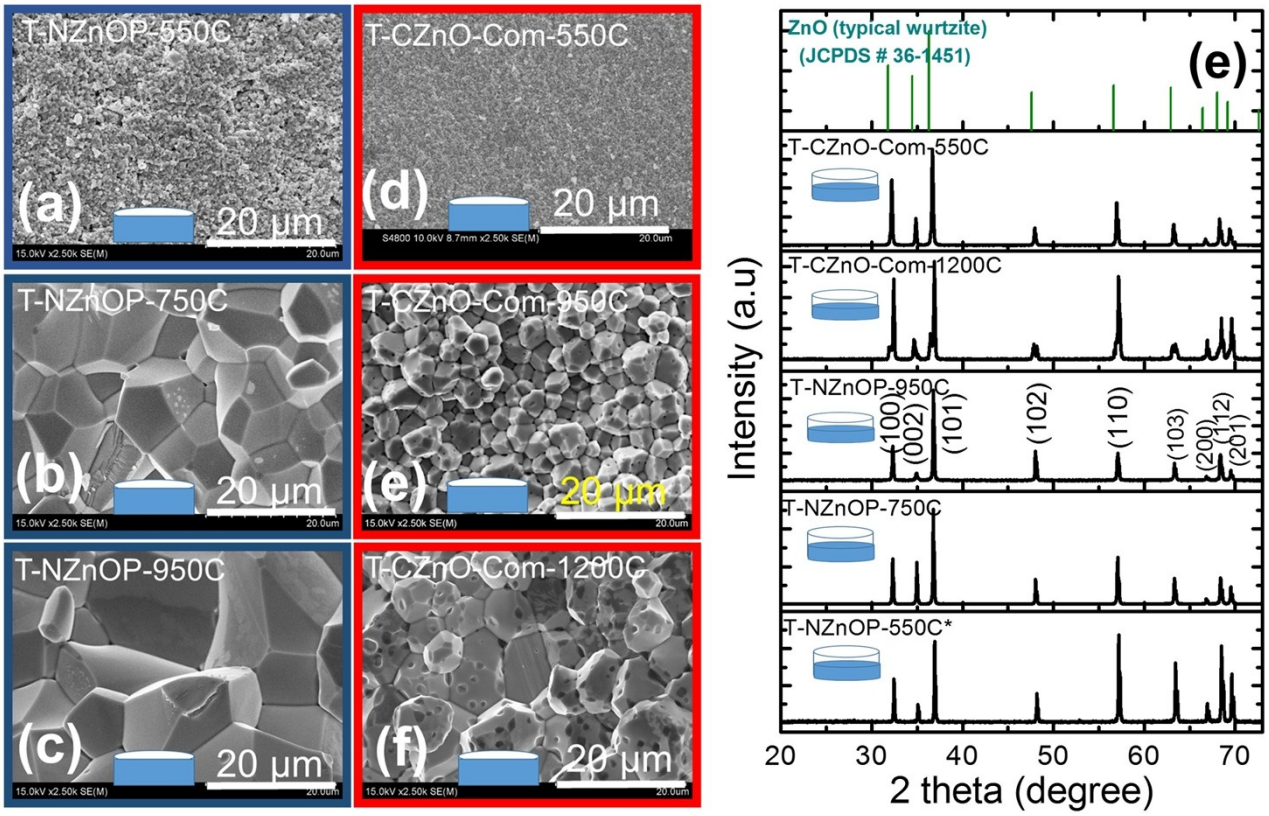


Fig.S7 Typical SEM micrograph images of the cross-sectional area of sample pellets of (a,b,c) T-NZnOP and (d,e,f) T-CNZnO-Com with (e) XRD pattern in different sintering temperature using low pressure SPS.

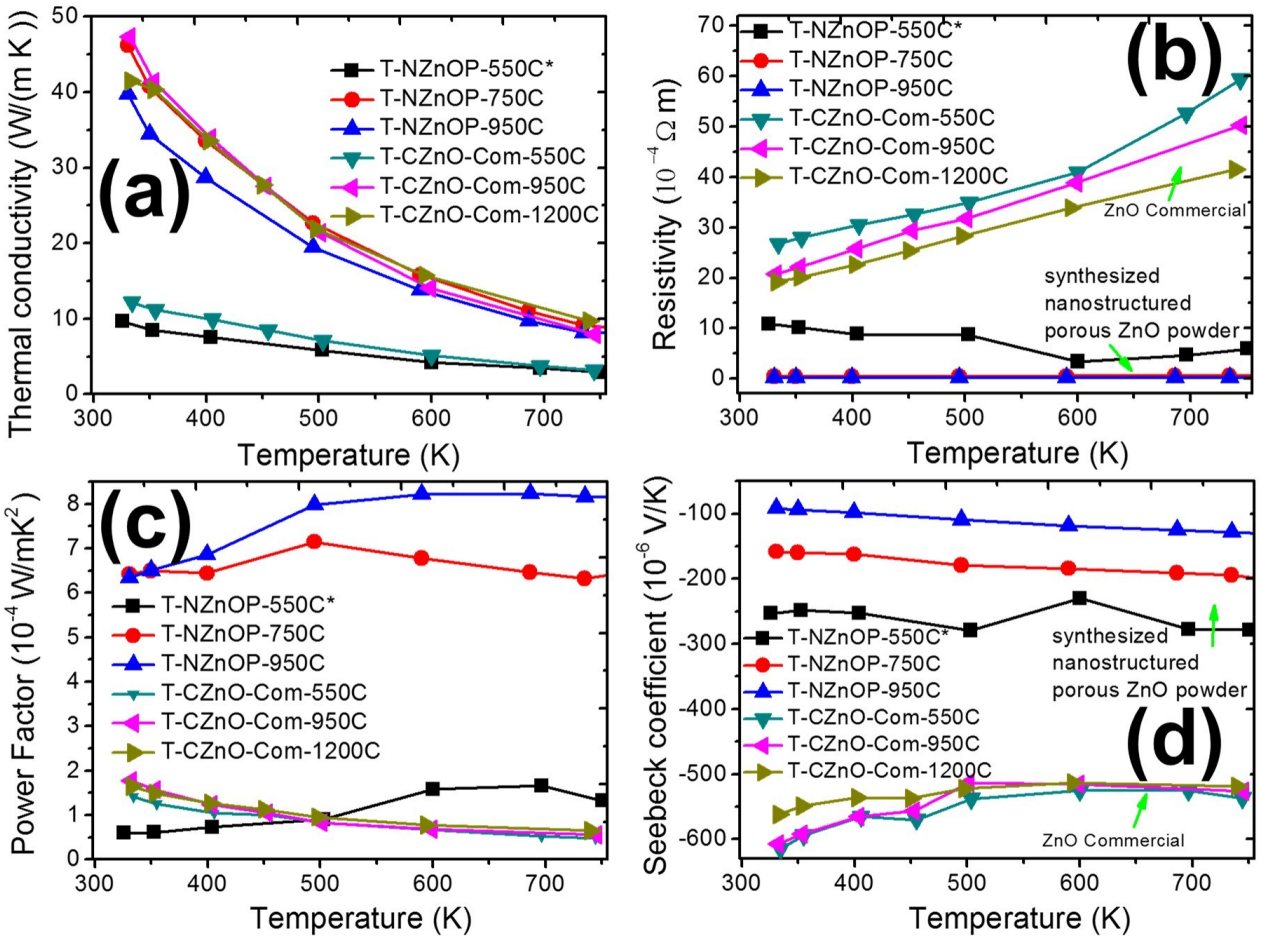


Fig.S8 Temperature-dependence of (a) thermal conductivity, (b) electrical resistivity, (c) Seebeck coefficient and (d) calculated powder factor for T-NZnOP and T-CZnO-Com series done after low pressured spark plasma sintering in Ar atmosphere.

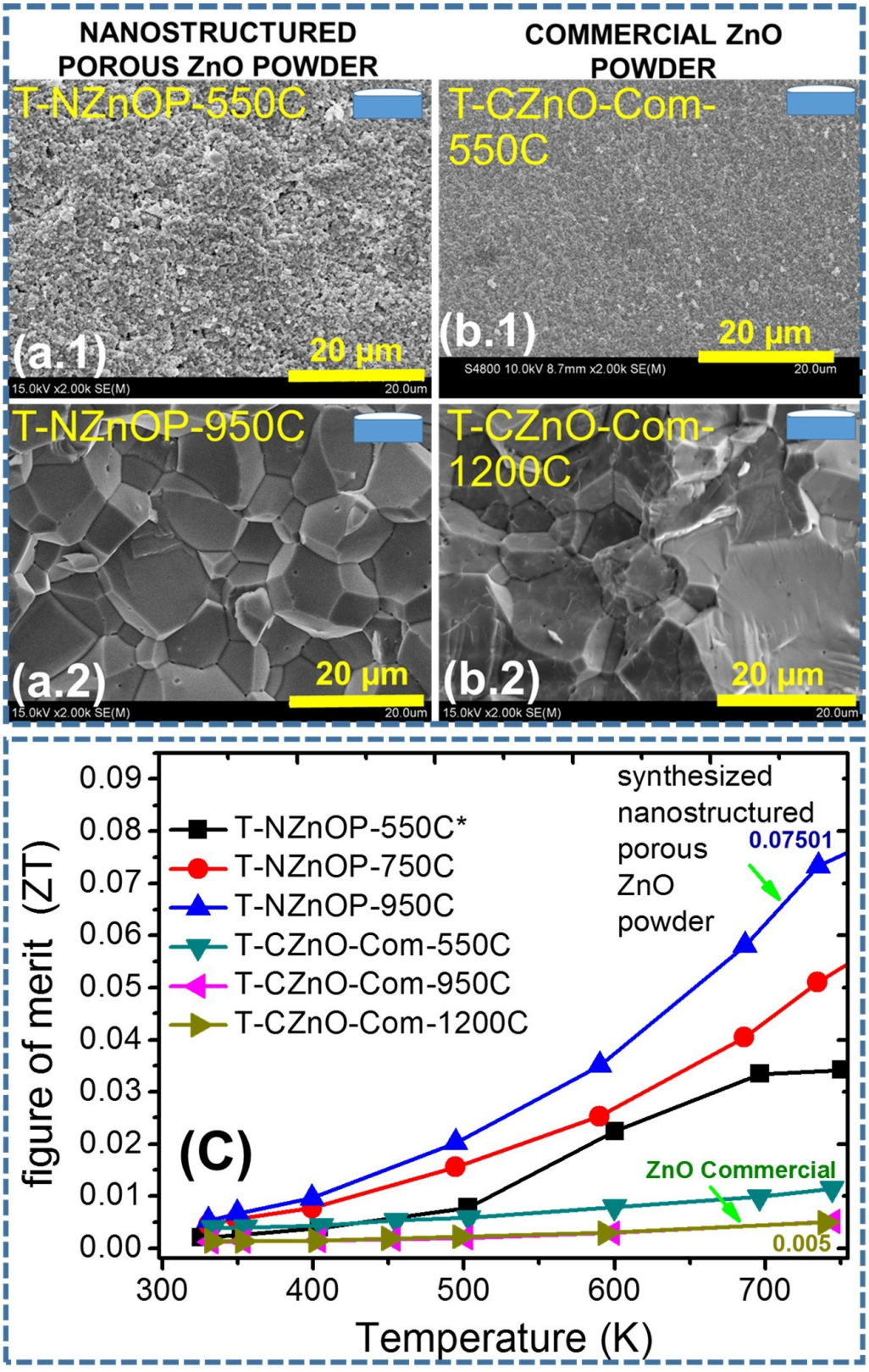


Fig.S9 Typical SEM micrograph cross sectional micrograph images with (c) Temperature-dependence of dimensionless figure of merit (*ZT*) of (a.1, a.2) T-NZnOP and (b.1, b.2) T-CZnO-Com.

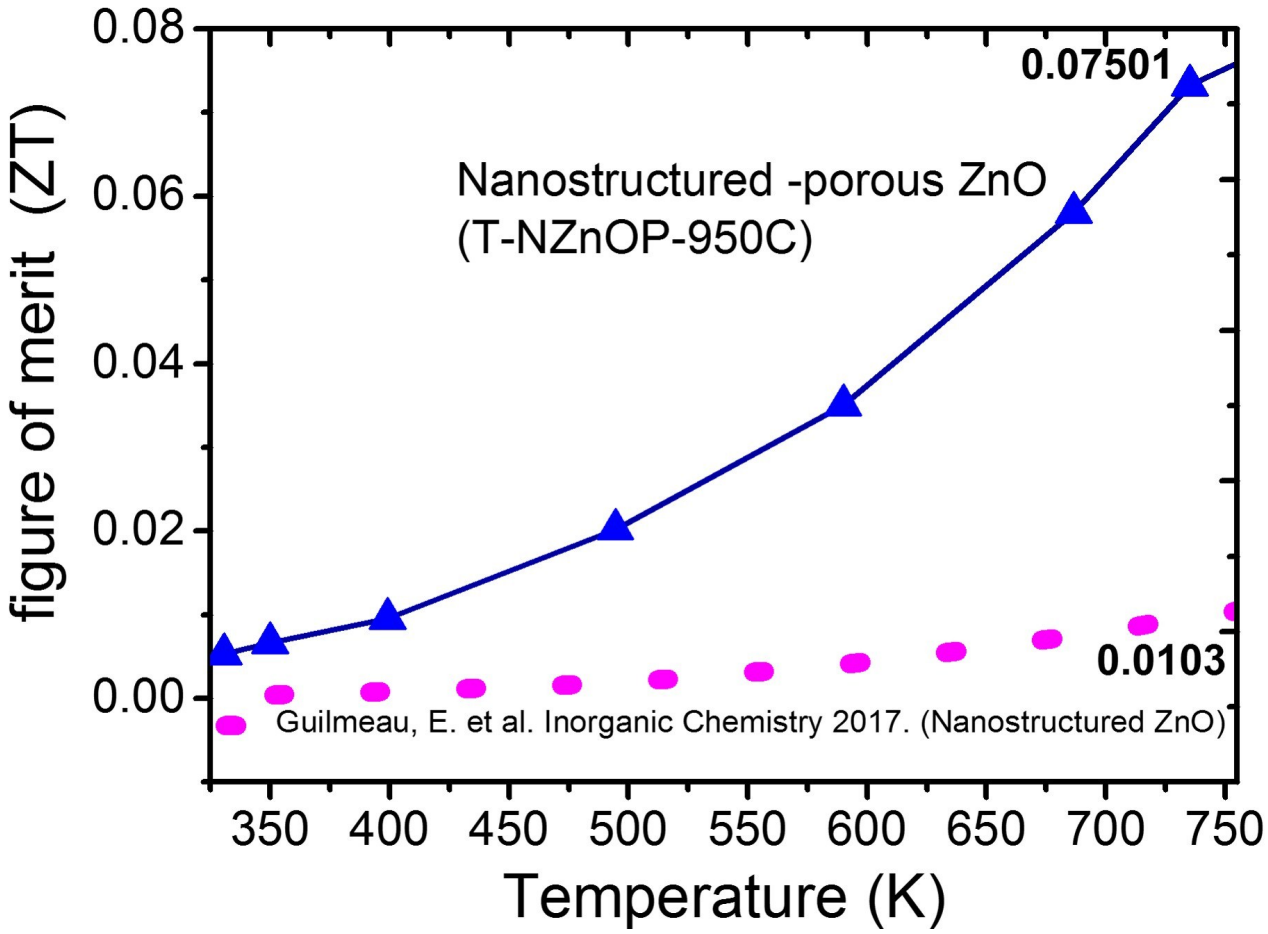


Fig.S10 Temperature-dependence of dimensionless figure of merit (*ZT*) of T-NZnOP-950C and referred (scaled based from Ref.7) ZnO-nanostructured data.