Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Flexible thermistors: pulsed laser induced liquid phase sintering of spinel Mn-Co-Ni oxide films on polyethylene terephthalate sheets

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Temperature variations during laser irradiation can be described by the heat diffusion equation simplified to describe one-dimensional heat flow:[1]

$$\rho C\frac{\partial T}{\partial t}=\kappa\frac{\partial^2 T}{\partial z^2}+\alpha I(z,t)$$

where T is the temperature function at time t and depth z, ρ is the mass density, C is the specific heat capacity, α is the optical absorption coefficient, κ is the thermal conductivity, and $I(z,t)$ is the laser power density. The laser power $I(z,t)$ is given by:

$$I(z,t)=I_0(t)\cdot(1-r)\cdot\exp(-\alpha z)$$

where r is the reflectance. The contribution from the incremental absorbance of the films caused by reflectance at the substrate surface was also included in the laser power distribution. $I_0(t)$ is described as a smooth pulse approximated by:

$$I_0(t)=I_0\cdot\left(\frac{t}{\tau}\right)^{\beta}\cdot\exp\left(\beta\left(1-\frac{t}{\tau}\right)\right)$$

where I_0 is the incident pulse power density, τ is the pulse duration (KrF: 26 ns), and β determines the temporal pulse shape (KrF: 6.0). We carried out numerical simulations for the temperature variation for the excimer laser irradiation process using a difference approximation based on the above equations. The initial conditions were T = 25 °C at t = 0 s and T = 25 °C at the bottom of the substrate. The boundary condition was $\kappa\frac{\partial T}{\partial z}=0$ at the interfaces. The physical constants used in the calculations are listed in Table S1.

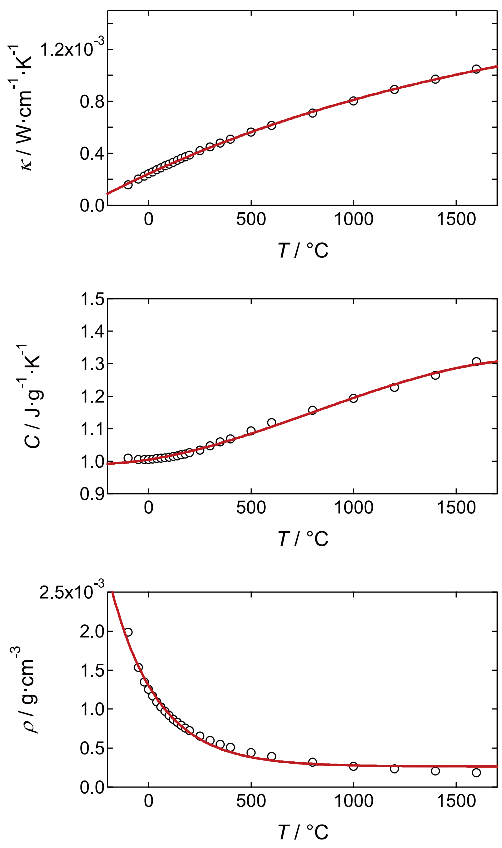

Fig. S1: The thermal conductivity, mass density and heat capacity of air.[2] The red lines represent the fitting curves.

Table S1 Physical properties used in numerical simulations.[2–4]

Material	α / cm^{-1}	r	κ / Wcm^{-1}K^{-1}	ρ / g cm^{-3}	C / Jg^{-1}K^{-1}
Mn_3O_4	9.58×10^4	0.191	0.057	4.856	0.624
Air	3.34×10^{-6}	0.00186	$1.57–10.5\times10^{-4}$	$0.18–1.98\times10^{-3}$	1.009–1.306

The thermal conductivity, mass density and heat capacity of air were obtained by the fitting of data from -100 ~ 1600 °C (Fig. S1).

Figure S2 shows the FESEM image for the MCN film that was irradiated by KrF laser at 55 mJ·cm^{-2} for 50 pulses. The small nano-particles on the surface and nano-pores were clearly confirmed. Conversely, such kind of nanostructures was not observed in the MCN film prepared by the MCN dispersion without the MCN-solution (Fig. S3).

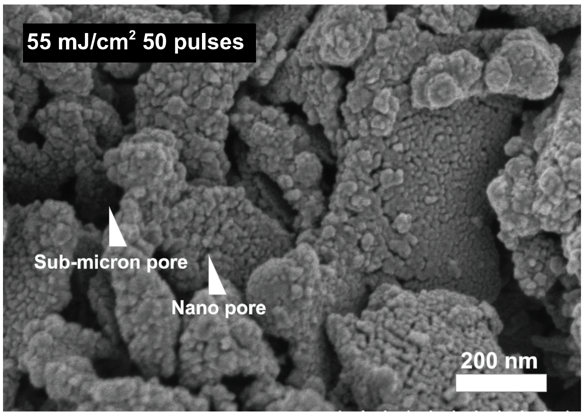

Fig. S2: The enlarged view of FESEM image for the MCN film irradiated at 55 mJ·cm^{-2} for 50 pulses.

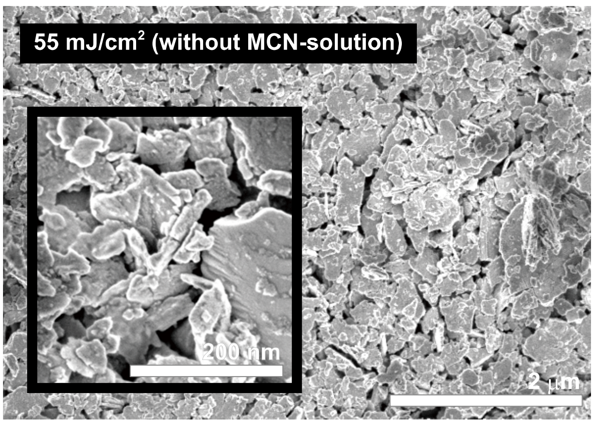

Fig. S3: The FESEM image for the MCN film coated by using the starting MCN dispersion without the MCN-solution, which irradiated at 55 mJ·cm^{-2} for 600 pulses.

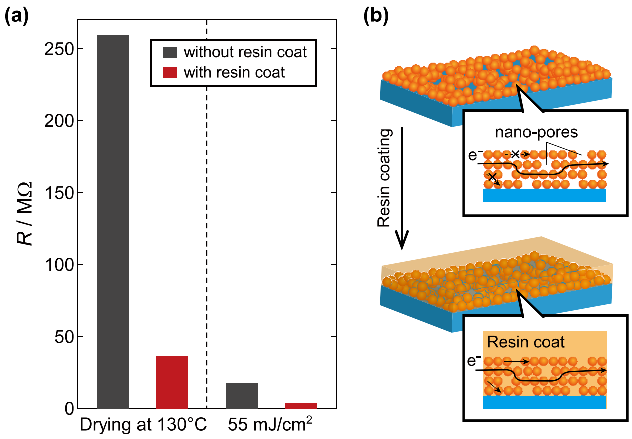

Fig. S4: (a) Resistance of MCN-T and MCN-L films before/after resin coating. (b) Schematic illustration for the contribution of resin coat to the electric carrier transport.

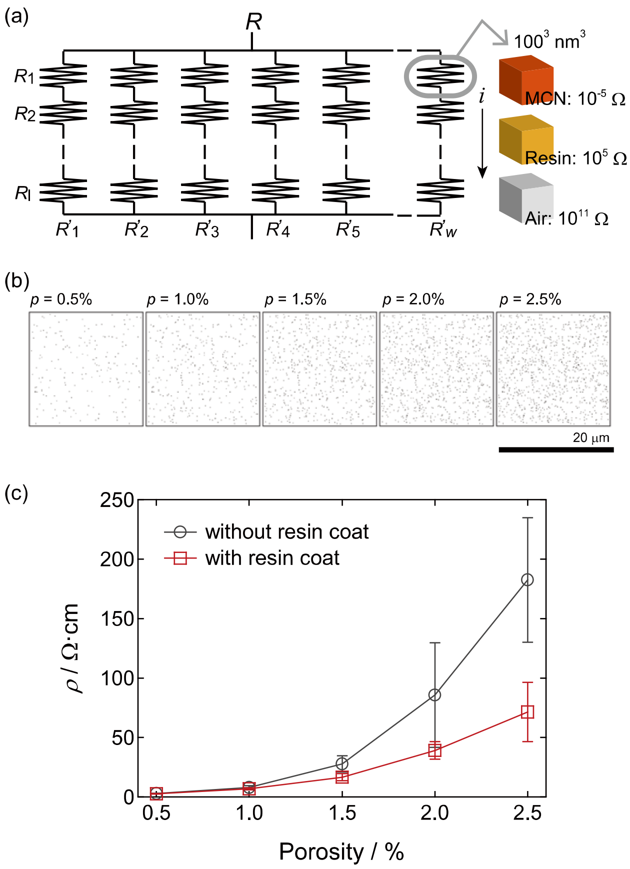

Fig. S5: (a) The electrical resistivity calculation model using simple serial-parallel circuit. (b) Randomly produced pores from 0.5–2.5 % in 20 μm × 20 μm × 100 nm. (c) The calculated electrical resistivity for the MCN layer with/without resin coat.

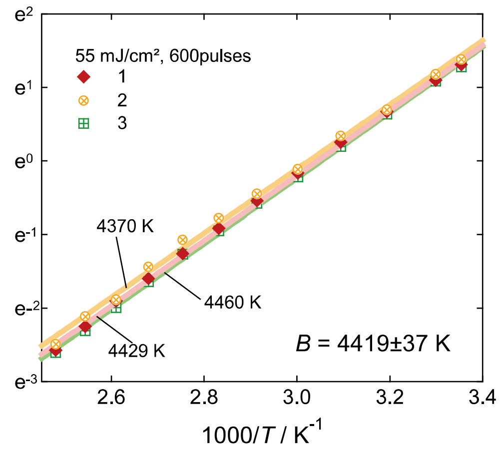

Fig. S6: Temperature variation of the electrical resistance, R (MΩ), for the three MCN films on PET substrates prepared at 55 mJ·cm^{-2} for 600 pulses. The solid lines are Arrhenius equation fitting curves.

Figure S4 shows the electrical resistance of MCN-T and MCN-L films before/after the resin coating. The coated resin filled the nano-pores, and they would contribute the resistance reduction. The electrical resistivity of MCN layer with the pores was calculated by using a simple serial-parallel circuit model as shown in Fig. S5a. We assumed the MCN layer with the cuboid size of 20 μm × 20 μm × 100 nm, which consisted of 100 nm cube resistive elements. The resistance of each element for MCN, resin (methylcellulose) and pore (air) were 10^{-5} Ω, 10^{5} Ω and 10^{11} Ω, respectively. The pores were produced randomly in the matrix for 0.5–2.5% (Fig. S5b). The calculation showed the difference of resistivity between the models with/without the resin coat. When the pore density (p) was sufficiently small ($p \leq 0.5\%$), the difference was ignorable. However, it much increased with the increasing p (≈ increasing pore number and size). This would reflect the experimental result as shown in Fig. 4a. Too large p ($p \geq 2.5\%$) caused complete disconnection of conduction pathways (MCN) and the resistivity was calculated to be huge (= insulator).

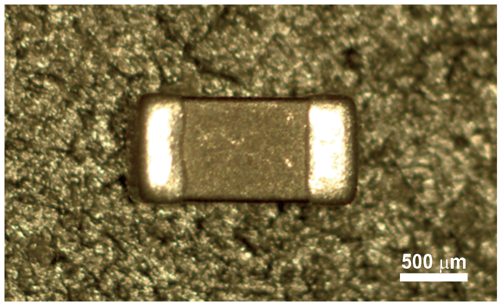

Fig. S7: The chip thermistor used for the temperature sensing test.

References

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