Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Interconnection of organic-inorganic hybrid nano-building blocks towards thermally robust mesoporous structures

*Naoki Tarutani, * [a,b,c] Riona Sato,[b] Wataru Yamazaki,[b] Kiyofumi Katagiri,[a] Kei Inumaru,[a] Takamasa Ishigaki [b,c]*

[a] Applied Chemistry Program, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan.
[b] Department of Chemical Science and Technology, Faculty of Bioscience and Applied Chemistry, Hosei University, 3-7-2 Kajino-cho, Koganei, Tokyo 184-8584, Japan.
[c] Research Center for Micro-Nano Technology, Hosei University, 3-11-15 Midori-cho, Koganei, Tokyo 184-8584, Japan.

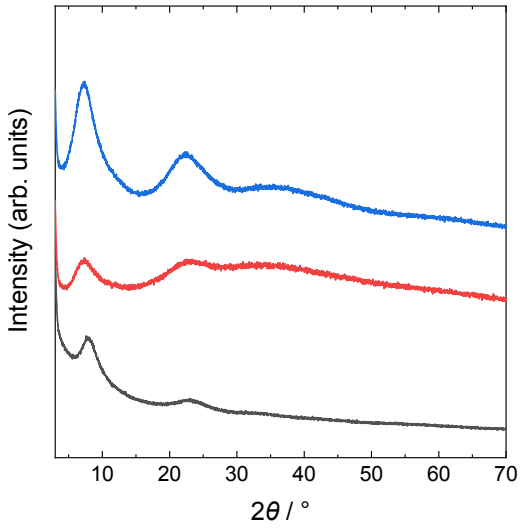

Fig. S1 XRD patterns of as-dried powders of acrylate-intercalated layered manganese (black), cobalt (red), and nickel (blue) hydroxides.

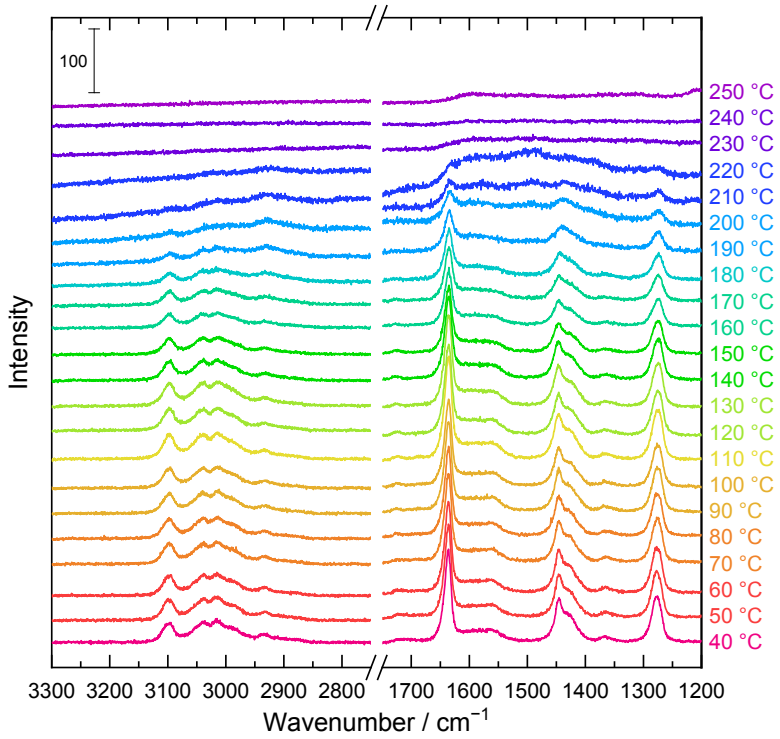

Fig. S2 *In situ* Raman spectra of acrylate-intercalated layered nickel hydroxide powder. Spectra between 3300–2700 cm^{-1} and 1800–1200 cm^{-1} were taken at 10 °C intervals from 40 °C to 250 °C (ramp rate of 20 °C/min and hold time at a specific temperature of 5 min). The bands assigned as $\nu(CH_2)_{as}$, $\nu(CH_2)_s$, and ν(CH) derived from the acrylate monomer disappeared and the band assigned as ν(CH) derived from the polymeric species was very weak in the spectrum heat treated at 200 °C, which is different from the results shown in Figure 4. The differences arise from the heat treatment condition. Hold time of 5 min was short to complete polymerization, which means the induction period may be longer than the minute scale.

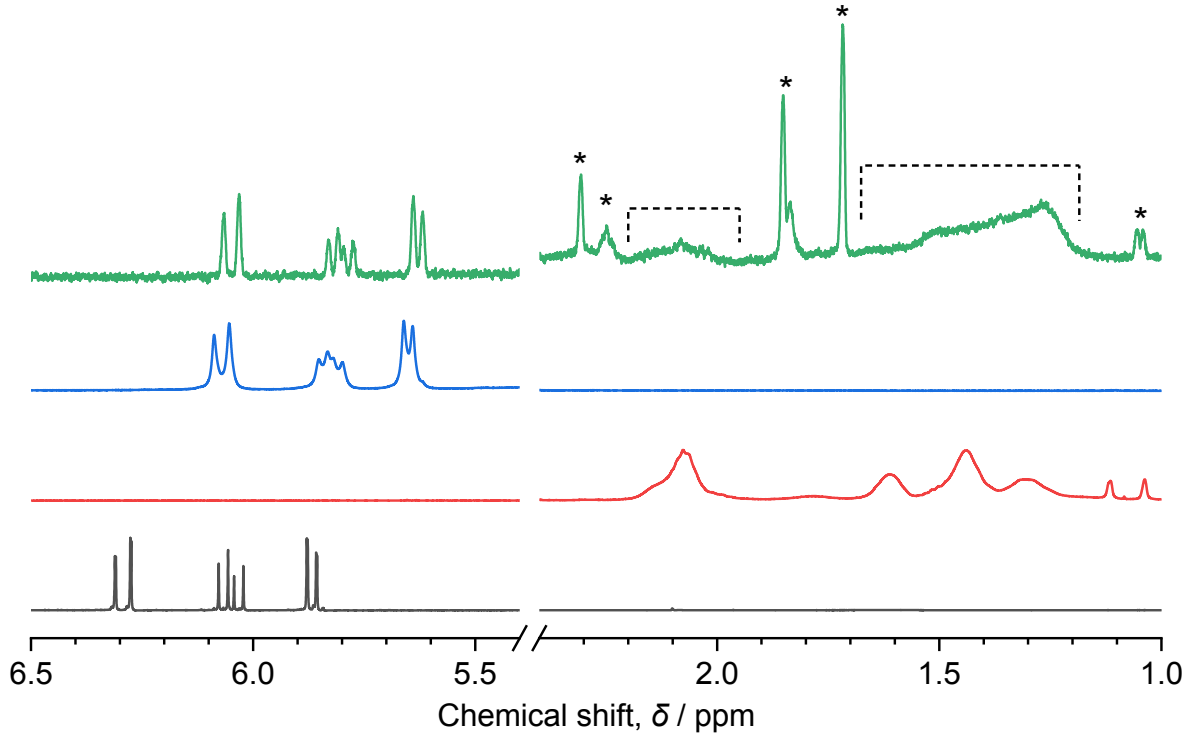

Fig. S3 NMR spectra of solutions dissolved acrylic acid (black), poly(acrylic acid) (red), as-dried (blue) and heat treated at 200 °C (green) layered nickel hydroxide powders. The signals assigned as monomer were shifted because of deprotonation.[1] Dash line region and * marks indicate signals derived from polymeric and oligomeric species, respectively. The signals of oligomeric species were assigned using ChemDraw NMR prediction tool.

1 A. Rojas-Hernández, E. L. Ibarra-Montaño, N. Rodríguez-Laguna and A. Aníbal Sánchez-Hernández, *J. Appl. Solut. Chem. Model.*, 2015, **4**, 7–18.

Table S1 Band position assignment of IR and Raman spectra.

As-dried powder		Heat treated powder at 200 °C		Sodium acrylate		Poly(acrylic acid sodium salt)		Assignment
IR / cm^{-1}	Raman / cm^{-1}	IR / cm^{-1}	Raman / cm^{-1}	IR / cm^{-1}	Raman / cm^{-1}	IR / cm^{-1}	Raman / cm^{-1}	
3098	3100	3118	3099	3087	3088			$\nu(CH_2)_{as}$
3031	3040			3044	3044			$\nu(CH_2)_s$
	3015 2994		3019	3013	3014			ν(CH)
2980				2979	2980			ν(C=C) + ν(C−C)
						2979	2982	
						2937	2926	ν(CH) or $\nu(CH_2)$
2921		2927	2929	2927				$\nu(COO)_{as}$ + δ(CH)
	2883		2780		2910 2903	2878	2916	–
						1751	1735	ν(COOH)
			1726					$\nu(C=C)_{op}$
1713	1712					1703		$\nu(C=O)_{op}$
		1670						–
1639	1637	1639	1637	1636	1636			$\nu(C=C)_{ip}$
		1597	1601				1601	–
1540	1574	1542		1551 1544	1551 1547	1565 1548	1571	$\nu(COO)_{as}$
			1501					–
						1454	1458	$\delta(CH_2)$
	1447		1435	1453	1458			$\nu(COO)_s$
				1439	1438			CH_2 scissors
1418	1428	1426		1414	1422			$\nu(COO)_s$
		1398	1407			1400	1415	ν(C−O)
1353	1363	1355		1361	1368			δ(CH)
1338				1339				–
		1314	1311			1325	1339 1304	$\omega(CH_2)$ or $\tau(CH_2)$
				1280	1285			ν(C−C)
1271 1195	1278	1273 1211	1275 1199	1271		1273		–
						1178	1191 1180	$\omega(CH_2)$ or $\tau(CH_2)$
						1138		–
		1097	1121			1106	1109	ν(C−C)
							1074	–
1062	1069	1059			1061			$\rho(CH_2)$

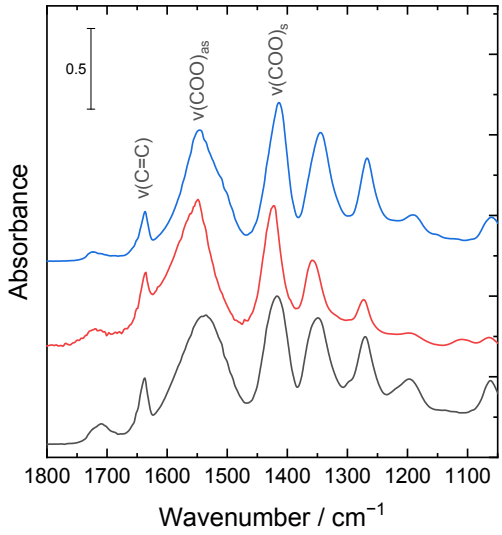

Fig. S4 IR spectra of layered nickel hydroxide powders; (black) as-dried, (red) heat treated at 150 °C for 20 h under air atmosphere, and (blue) heat treated at 200 °C for 2 h under vacuum condition.

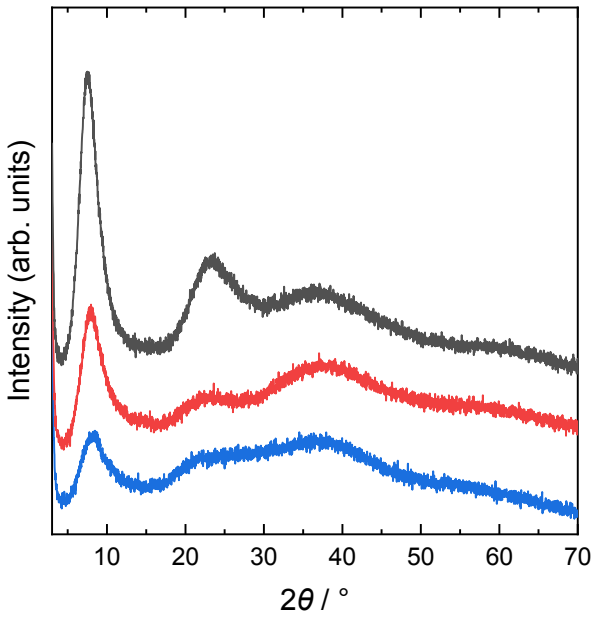

Fig. S5 XRD patterns of layered nickel hydroxide powders; (black) as-dried, (red) heat treated at 200 °C for 2 h, and (blue) heat treated at 200 °C for 2 h and 250 °C for 6 h.

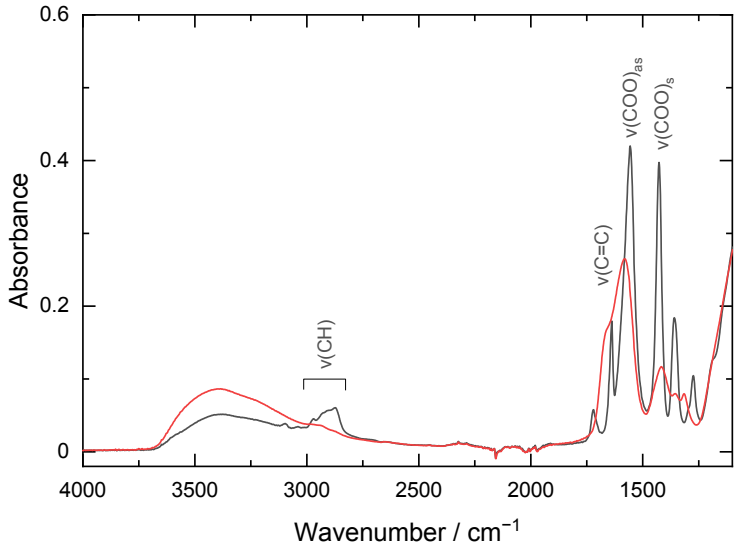

Fig. S6 IR spectra of films as spin-coated (black) and heat treated at 200 °C (red). The bands around 2870−2970 cm^{-1} are assigned to ν(CH) of the F127 block copolymer.

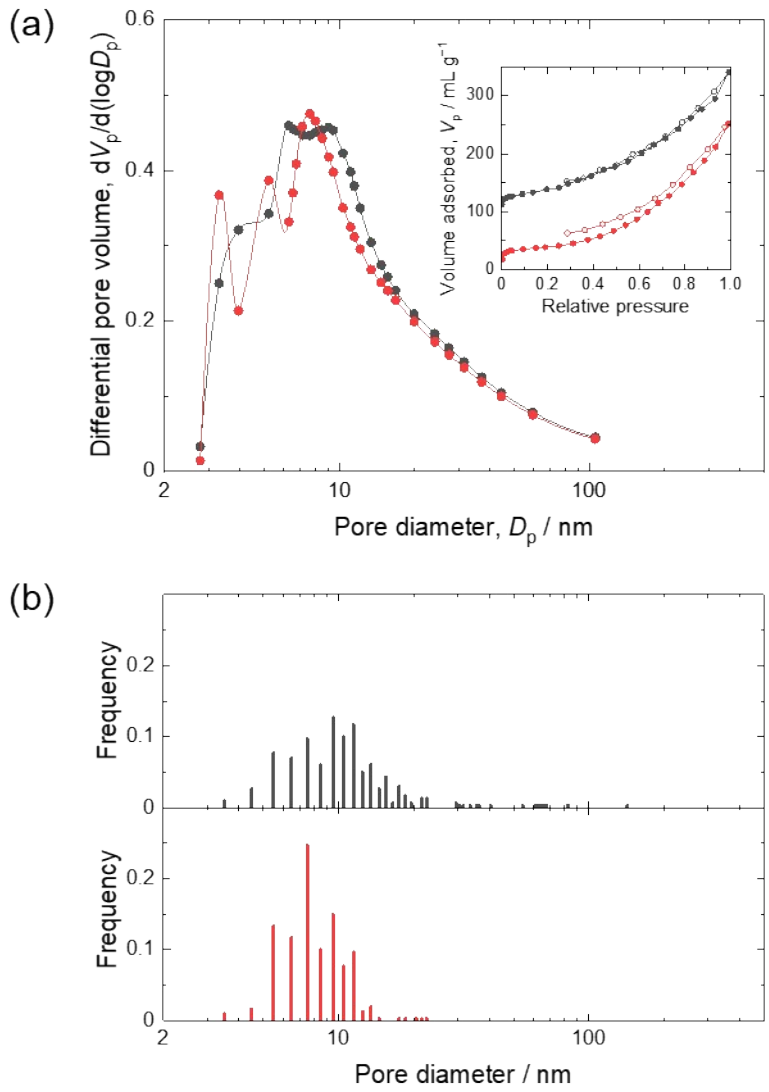

Fig. S7 (a) BJH pore size distributions and (b) pore size distributions measured from SEM images of the film prepared through (black) one-step heat treatment 250 °C for 6 h and (red) two-step heat treatment at 200 °C for 2 h and 250 °C for 6 h. Inset of (a) is N_2 adsorption-desorption isotherms. The diameters of 300 pores were measured for preparation of distributions in (b).

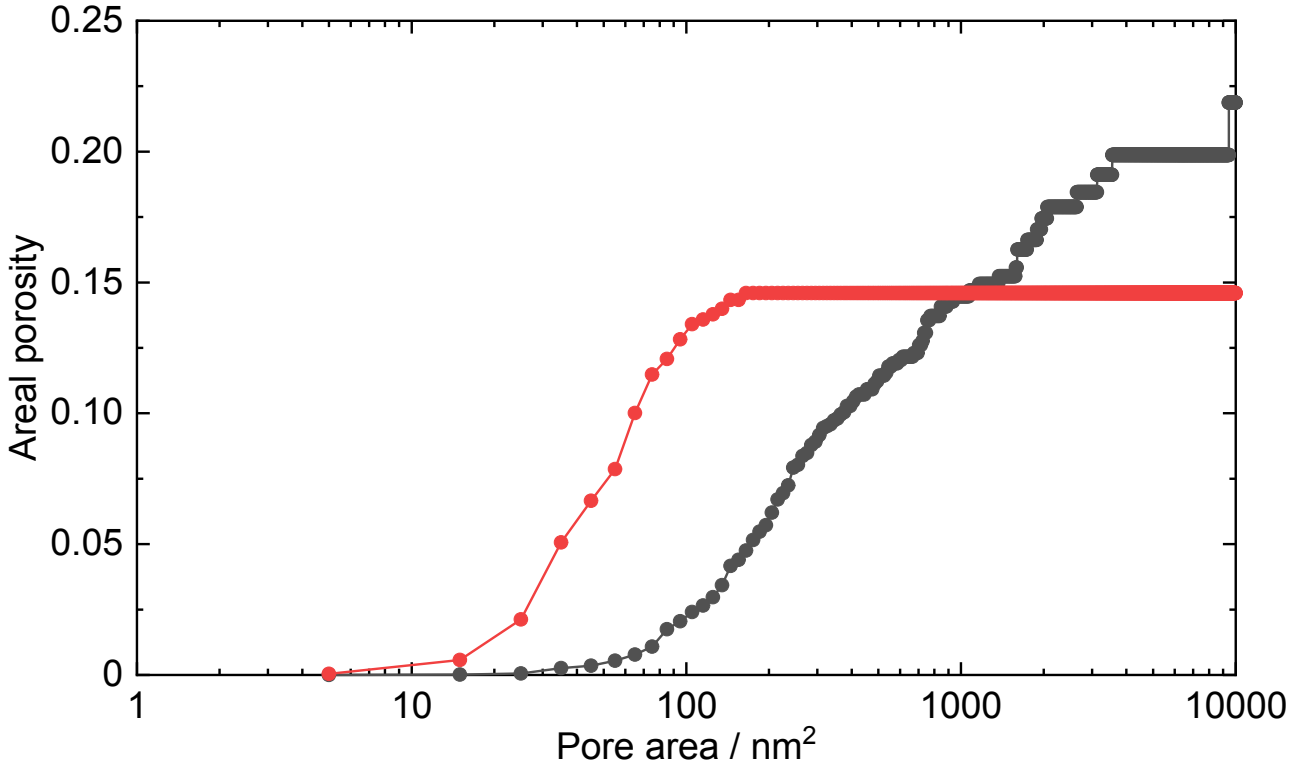

Fig. S8 Pore area distribution of the film prepared through (black) one-step heat treatment 250 °C for 6 h and (red) two-step heat treatment at 200 °C for 2 h and 250 °C for 6 h. The pore areas and areal porosity were determined by measuring about 400 pores.

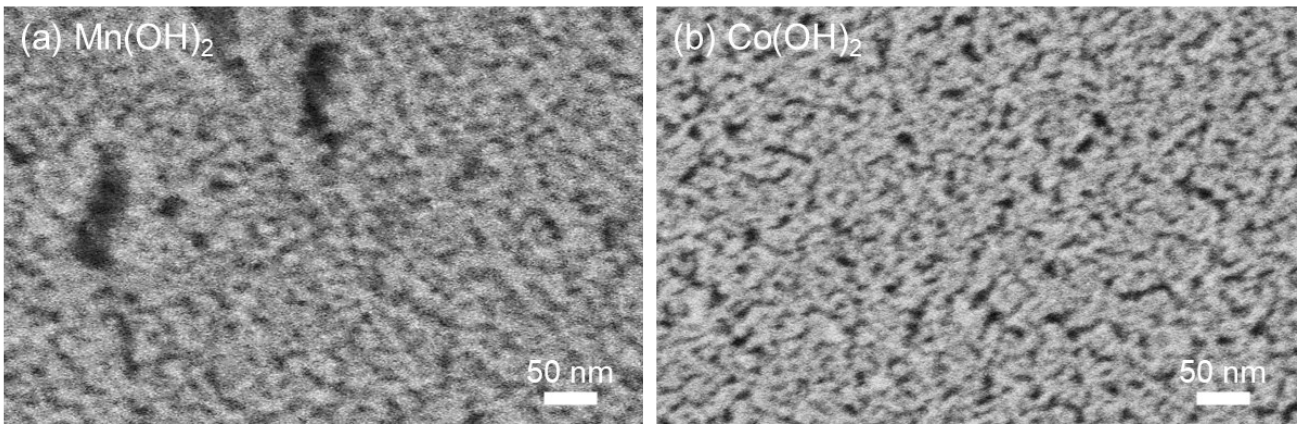

Fig. S9 SEM images of the films prepared through two-step heat treatment at 200 °C for 2 h and 250 °C for 6 h; (a) layered manganese hydroxide and (b) layered cobalt hydroxides. Insets are corresponding FFT images.

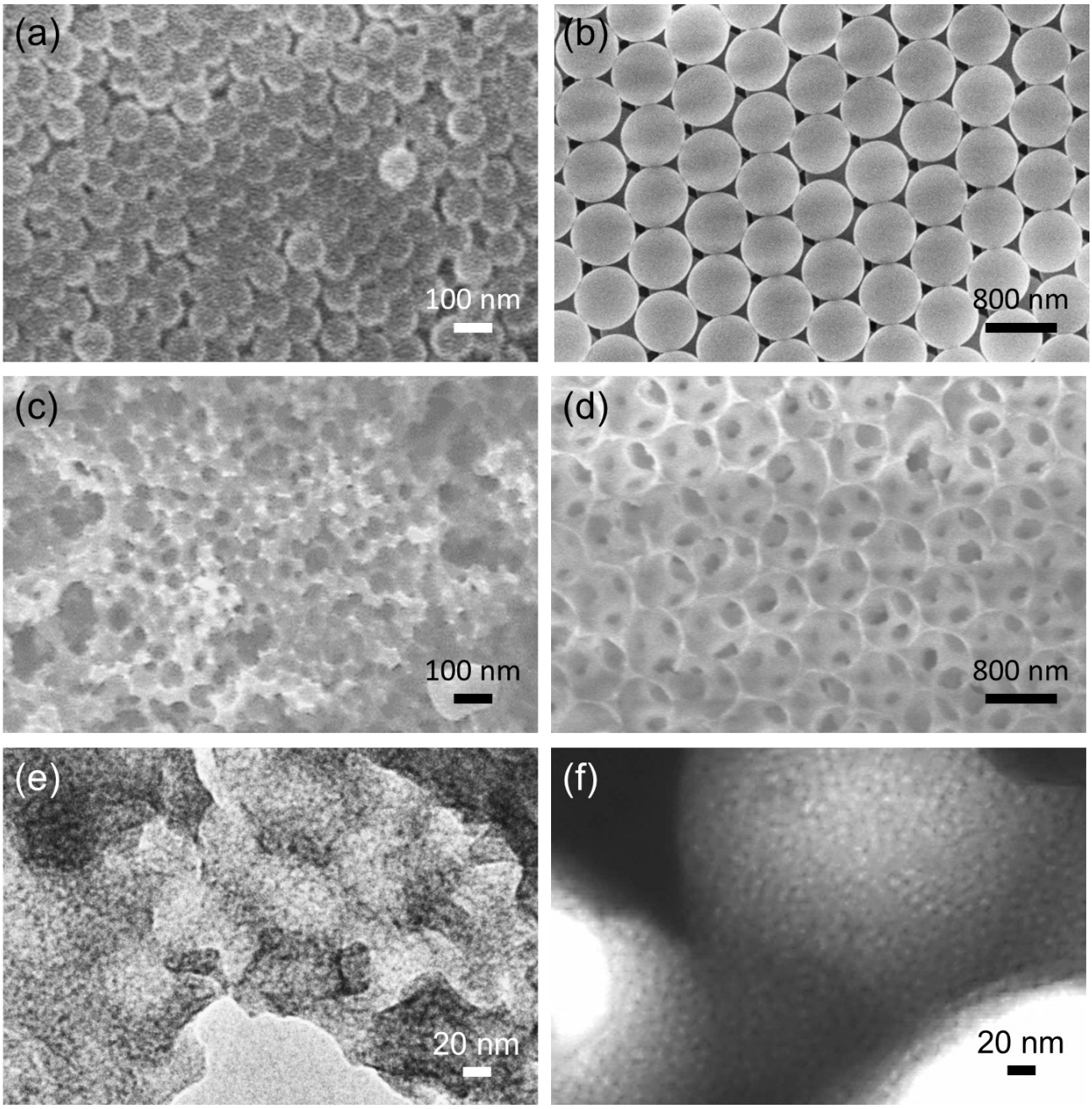

Fig. S10 SEM images of polystyrene latex templates with a particle diameter of around (a) 100 nm and (b) 720 nm. (c) (d) SEM, (e) TEM, and (f) STEM images of layered nickel hydroxides templated using polystyrene latex templates of (c) (e) 100 nm and (d) (f) 720 nm.

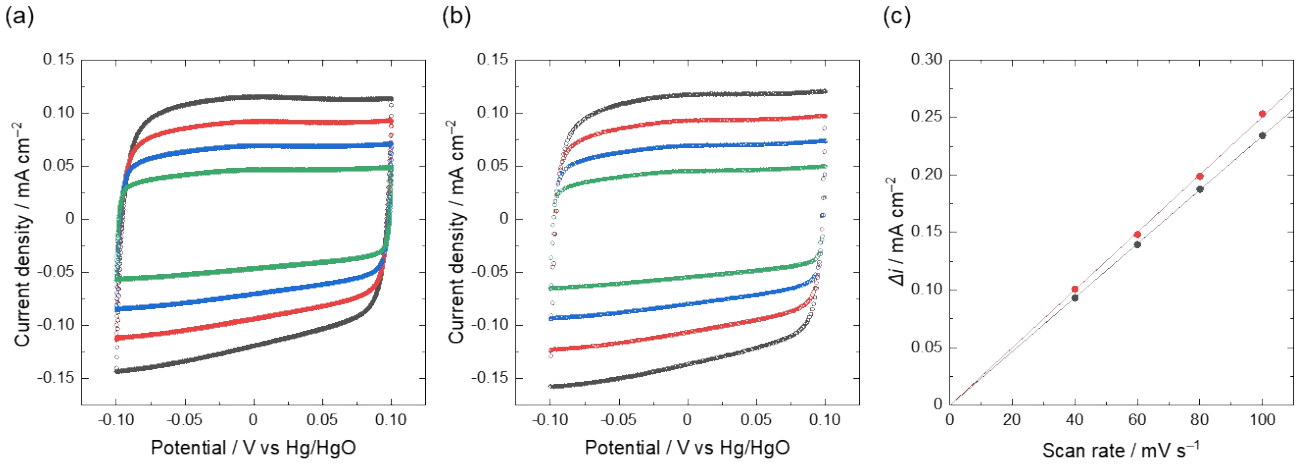

Fig. S11 Cyclic voltammetry curves of films prepared through (a) one-step heat treatment and (b) two-step heat treatment with scan rates of 100 (black), 80 (red), 60 (blue), and 40 mV s^{-1} (green). (c) Relation of Δ*i* and scan rate, where Δ*i* is difference of anodic and cathodic current density at 0 V (black: one-step heat treated film; red: two-step heat treated film).