Supporting Information

Nickel Oxide Encapsulated Nitrogen-rich Carbon Hollow Spheres with Multiporosity for High-Performance Pseudocapacitors Having Extremely Robust Cycle Life

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Experimental

Chemicals: Melamine, Formaldehyde (37 wt%), and CTAB (Cetyl trimethylammonium bromide) were purchased from Sigma-Aldrich. Sodium Hydroxide was purchased from JUNSEI. Water was purchased from Merck. Nickel Chloride 6-Hydrate was purchased from YAKURI Chemical. All chemicals were used as received in air.

Syntheses: Melamine (5.0448 g, 0.04 mol) and formaldehyde solution (8.924 ml, 0.12 mol) are mixed with 1M NaOH aqueous solution (0.2 ml) and CTAB (Cetyl Trimethylammonium Bromide, 4 g) in water (100 ml). Then, the mixed solution is heated under 373 K for 15 min to synthesize MF (Melamine-Formaldehyde) resin. Nickel(II) chloride hexahydrate (0.951 g, 0.004 mol) is dissolved in MF resin after cooling the solution. Ni precursors contained MF resin is sprayed from a nozzle by N_2 gas (Scheme 1), and droplets of the solution are gone through the furnace. The final particles are collected on a filter (Stericup 0.45 μm, Millipore). Since there are some remnants of MF resin on the surface of the particles, the products are washed with water-ethanol mixed solution (1:1 volume ratio) and filtered. The final particles are designated as 6N, 7N, and 8N, where the temperatures of the furnace are 673, 773, and 873 K, respectively. The color of each sample is light green, brown, and dark brown for 6N, 7N, and 8N. Heat treatments of the products are performed in H_2 atmosphere under 673 K for 3 hours, and they are named as 6NH, 7NH, and 8NH1. 8N was heat treated in N_2 for 4 hours under 773 K while the ramping rate is 1 K/min, and the product is designated as 8NH2.

Analyses: SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy) were carried out on a Hitachi S4800 and FEI Tecnai F20 Microscope, respectively. X-ray photon spectroscopy (XPS) data were collected with an ESCALAB 250 using a monochromatized Al (Kα) source. N_2 adsorption-desorption isotherms were carried out using a Quantachrome Instruments Autosorb-1c apparatus at 77 K, respectively. 8N and 7NH were outgassed at 333 K and 8NH2 was outgassed at 373 K for 24h before measurements. X-ray diffraction patterns were obtained by Rigaku D/max-IIIC (3kW) with Cu Kα radiation. The capacitive performance was measured with a three-electrode device consisting of a platinum wire, a SCE, and samples as the counter, reference, and working electrodes, respectively. The working electrode was composed of the 90 wt% active material and the 10 wt% polyvinylidene fluoride (PVDF) binder on the nickel foil and by drying the sample in a vacuum oven at 80°C. The electrochemical system was assembled with the 1 M KOH aqueous electrolyte and was sealed with Parafilm. The CV and galvanostatic measurements of a surface Faradaic reaction were performed using a VSP potentiostat. The mass of total composites in the electrode was ~1.5 mg cm^{-2}, which was measured using a XP2U ultra-microbalance (d = 0.1 μg, Mettler Toredo).

Asymmetric capacitor: NG electrodes were prepared using the same method reported in our previous study. Graphite was first oxidized to graphene oxide (GO) by Hummer's method. The dried GO was reduced by a plasma enhanced chemical vapour deposition (PECVD) process. In this process, the GO is first reduced by a hydrogen plasma process (500 W in power, 4 torr of H_2 gas with 100 sccm in flow rate). Subsequently, after the reduction step, nitrogen plasma (500 W in power, 14 torr of N_2 gas with 91 sccm in flow rate) was introduced onto the graphene surfaces to complete NG. Finally, the samples were annealed at 300 ^{o}C for 3 hrs to remove residual functional groups on the NG surface. A slurry was first prepared by dissolving NG and PVDF (w:w=9:1) in NMP. The slurry was casted on nickel foil and dried in a vacuum oven overnight. Platinum leads were in contact with the back sides of the substrates in order to connect to an electrochemical tester (Bio-logic VSP). To investigate the properties of a negative electrode, the as-obtained NG for the negative electrode in a full-cell device were measured under a three-electrode cell configuration of a platinum wire, and an SCE electrode in a 1 M KOH. The CV and galvanostatic measurements were performed using a VSP potentiostat.

Based on the specific capacitance of each electrode and the principle of charge balance between two electrodes, the mass ratio of 8NH2 to the NG was determined to be 0.5. The total mass of active material on the negative electrode was 1.5 mg cm^{-2} while on the positive electrode it was 0.5 mg cm^{-2}. The electrochemical properties of the asymmetric full-cell device were investigated under a two-electrode cell configuration with 8NH2 as a positive electrode and NG as a negative electrode in 1 M KOH electrolyte solution. The CV and galvanostatic measurements were performed using a VSP potentiostat. The data analysis of the full-cell device is calculated by based on a total mass of samples for both electrodes.

Data Anlysis: In the galvanostatic data, the *IR* drop at the upper cut-off potential and slope in the discharge curve are used to obtain the average power and energy density. The specific capacitance (C_s) is calculated by using

$$C_s = I \ x \ \Delta t / (\Delta V \ x \ M)$$

in which *I* is the current applied, the slope is that of the discharge curve after the *IR* drop, and *M* is the total mass of material on both electrode. Similarly, energy density (*E*) is calculated using

$$E = 0.5CV^2 / M$$

in which *V* is the cut-off potential excluding the *IR* drop, *M* is the total mass of material on both electrode, and *C* is the measured capacitance.

The average power density is calculated by using

$$P = E / \Delta t$$

in which *E* is the energy density, and Δt is the discharge time after *IR* drop.

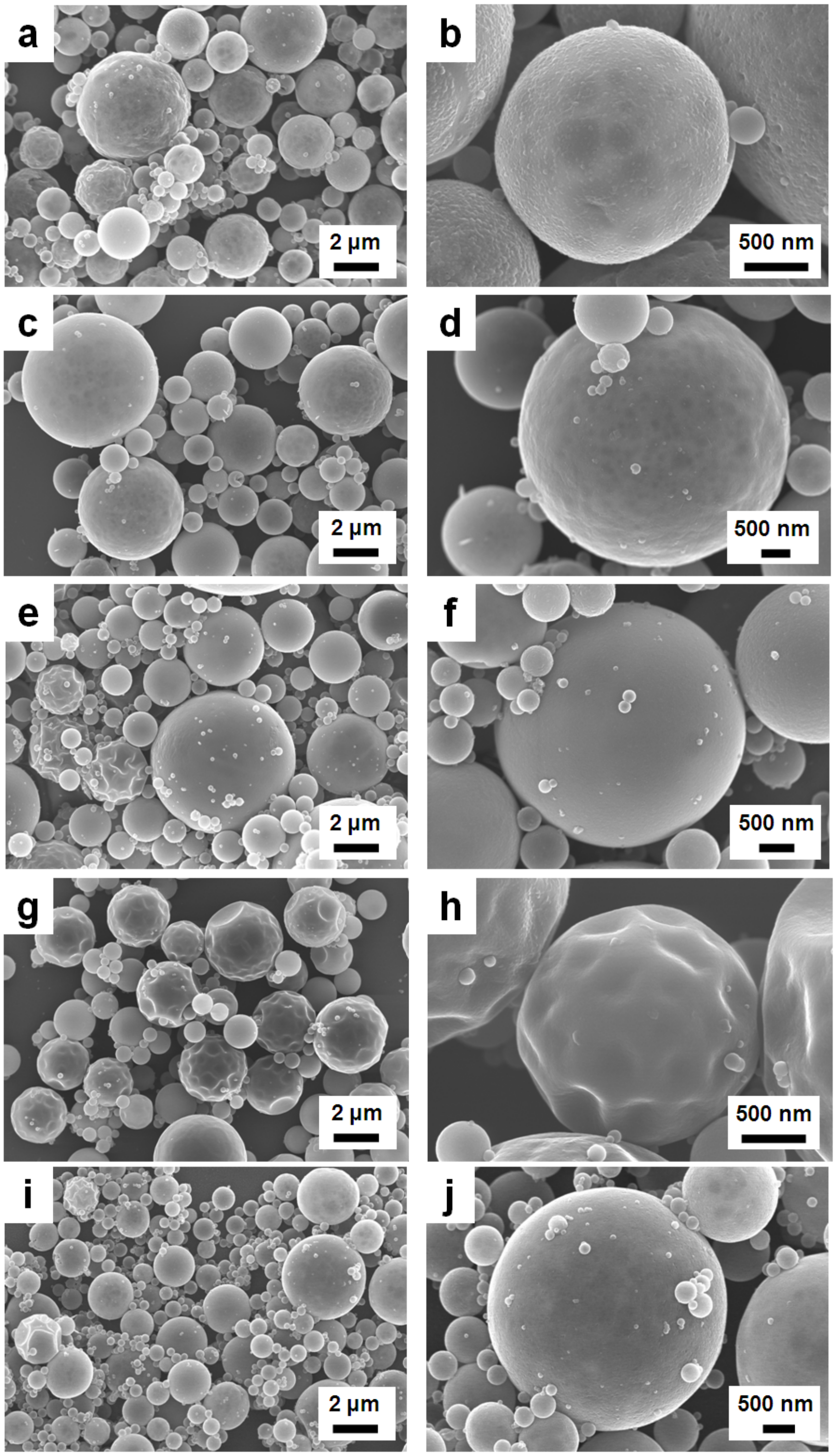

Figure S1. SEM images of nickel nitrogen-rich carbon spheres synthesized using the NSP (Nozzle Spray Pyrolysis) at 873 K with a-b) 5 at%, c-d) 10 at% (8N), e-f) 15 at%, and g-h) 30 at% of nickel atoms. i-j) SEM images of 8NH1 (Heat treated 8N in H_2 at 673 K).

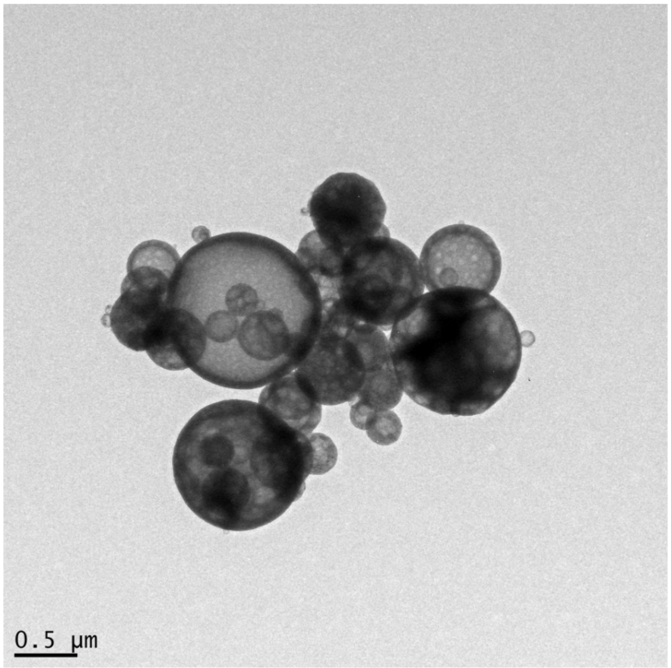

Figure S2. TEM image of 8N (hollow porous nickel nitrogen-rich carbon spheres synthesized using at the NSP at 873 K)

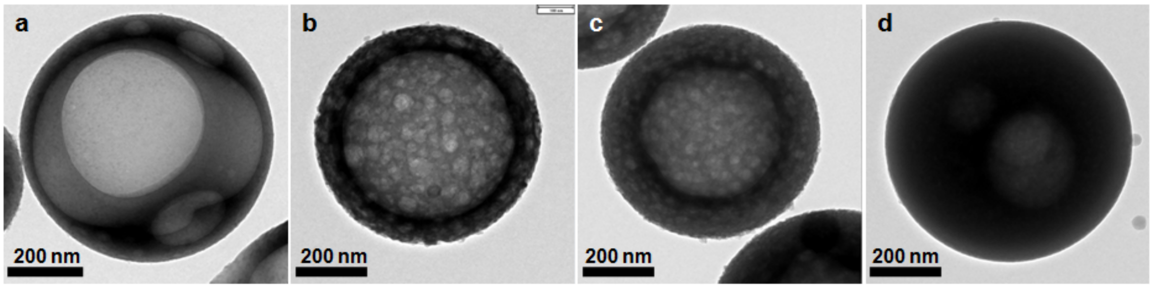

Figure S3. TEM images of hollow porous nickel nitrogen-rich carbon spheres synthesized using the NSP (Nozzle Spray Pyrolysis) at 873 K with a) 5 at%, b) 10 at% (8N), c) 15 at%, and d) 30 at% of nickel atoms.

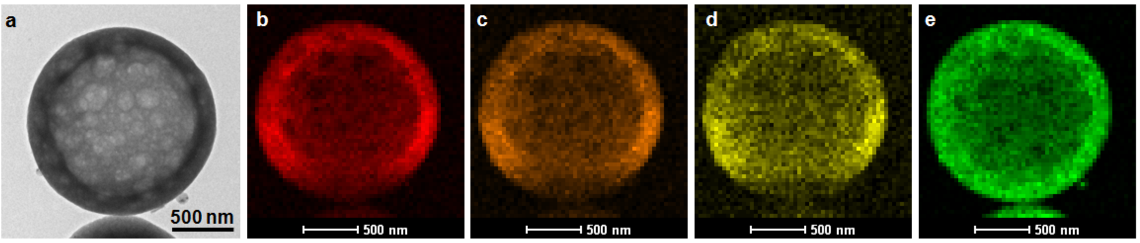

Figure S4. a) TEM image of 8N (hollow porous nickel nitrogen-rich carbon spheres synthesized using the Nozzle Spray Pyrolysis at 873 K). EDS mapping of elements b) carbon, c) nitrogen, d) oxygen, and e) nickel for the 8N.

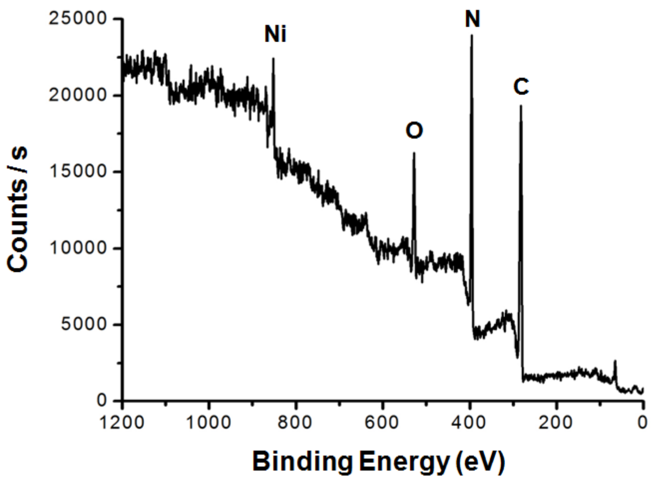

Figure S5. XPS of 8N (hollow porous nickel nitrogen-rich carbon spheres synthesized using at the NSP at 873 K)

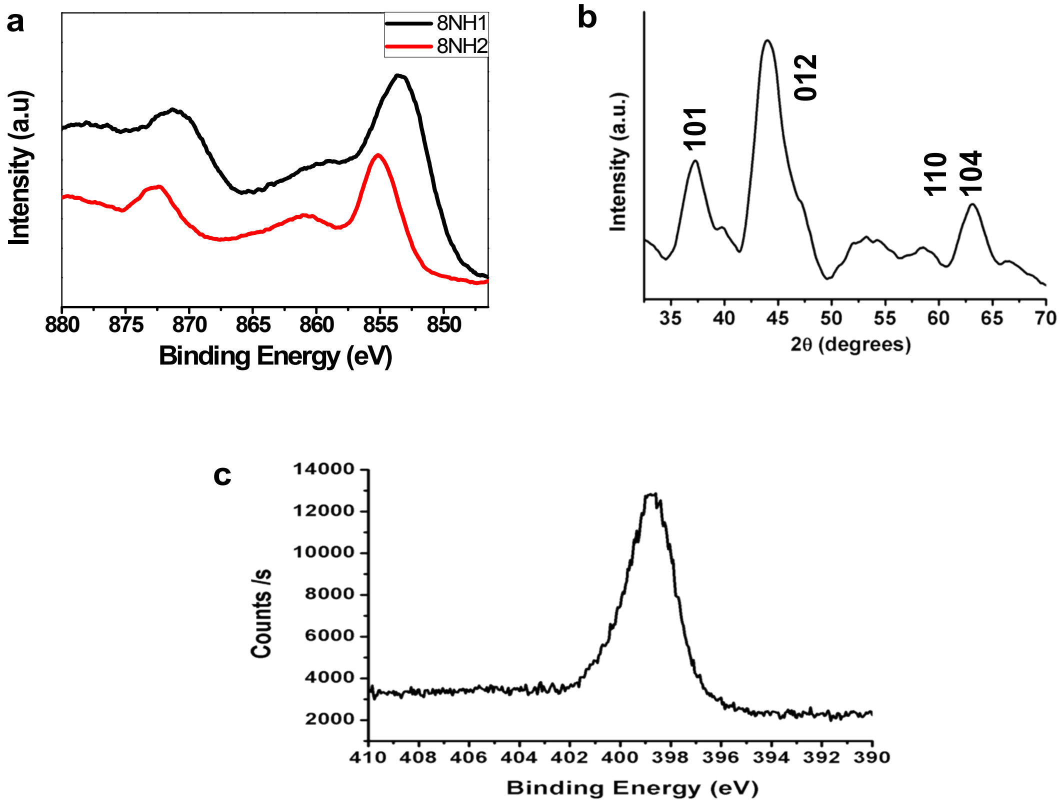

Figure S6. a) Ni-XPS data of 8NH1 that is a heat-treated nickel nitrogen-rich carbon hollow sphere under H_2 gas flow at 673 K), and 8NH2 that is a heat treated nickel nitrogen-rich carbon hollow sphere under N_2 gas flow at 773 K. b) A XRD pattern of 8NH2. The space group and space number of NiO in 8NH2 are R-*3mH* and 166, respectively. c) N1s XPS data of 8NH2.

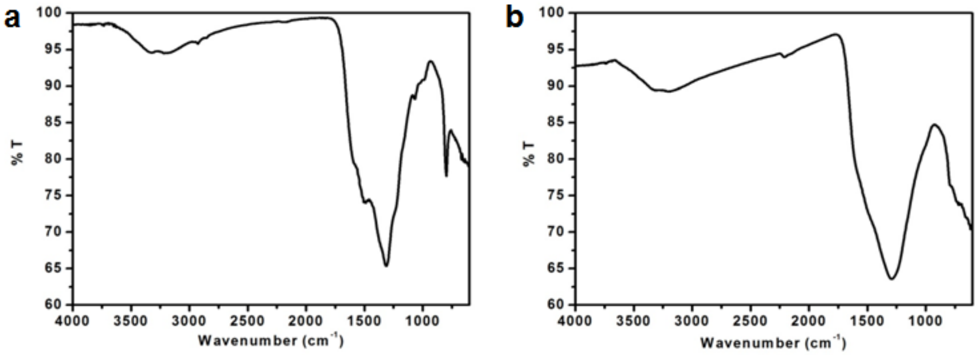

Figure S7. FT-IR spectra of a) 8N (hollow porous nickel nitrogen-rich carbon spheres synthesized using at the NSP at 873 K) and b) 8NH2 (Heat treated 8N in N2 at 773 K).

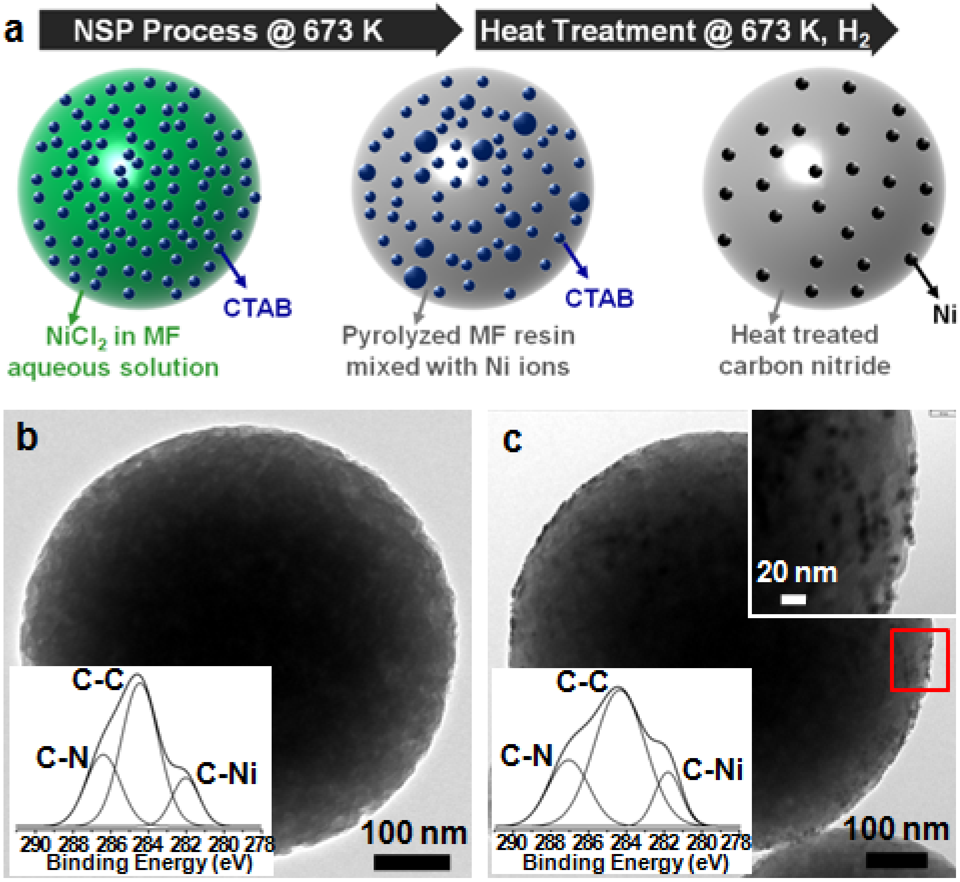

Figure S8. a) Schematic of the NSP (Nozzle Spray Pyrolysis) process at 673 K using Melamine-formaldehyde (MF) aqueous solution mixed with $NiCl_2$ and CTAB (cetyl trimethylammonium bromide). Green and blue represent MF/$NiCl_2$ aqueous solution and CTAB, respectively. Light greenish products are collected after the NSP process at 673 K and designated as 6N. b) TEM image of 6N shows no pore in the spheres, which implies that CTAB is not decomposed during the NSP process. Since the color of 6N is similar to that of the Ni precursor dissolved MF resin solution, most of the nickel atoms are assumed to exist in the spheres as an ion and physically mixed with MF resin throughout the products. The NSP process temperature of 673 K is not only too low for decomposing the CTAB, but also not energetically high enough to produce nickel-carbon bonds. The carbon 1s XPS data of 6N shows the lowest peak of C-Ni bonds among the 6N, 7N, and 8N particles (Inset of Fig. S8b) TEM image of 6NH, heat treated 6N in H_2 at 673 K , shows nanosized (< 10 nm) nickel particles inside of the products. During the heat treatment, the surfactants in the spheres are decomposed, but simultaneously the void spaces are collapsed by the additional reaction between unreacted MF resin molecules, resulting in porous solid spheres with the closed window. According to the carbon 1s XPS curves of 6NH, it seems that more C-Ni bonds are generated during the heat treatment since the peak intensity of C-Ni bond is slightly higher in the curve of 6NH than that of 6N (Inset of Fig. S8c).

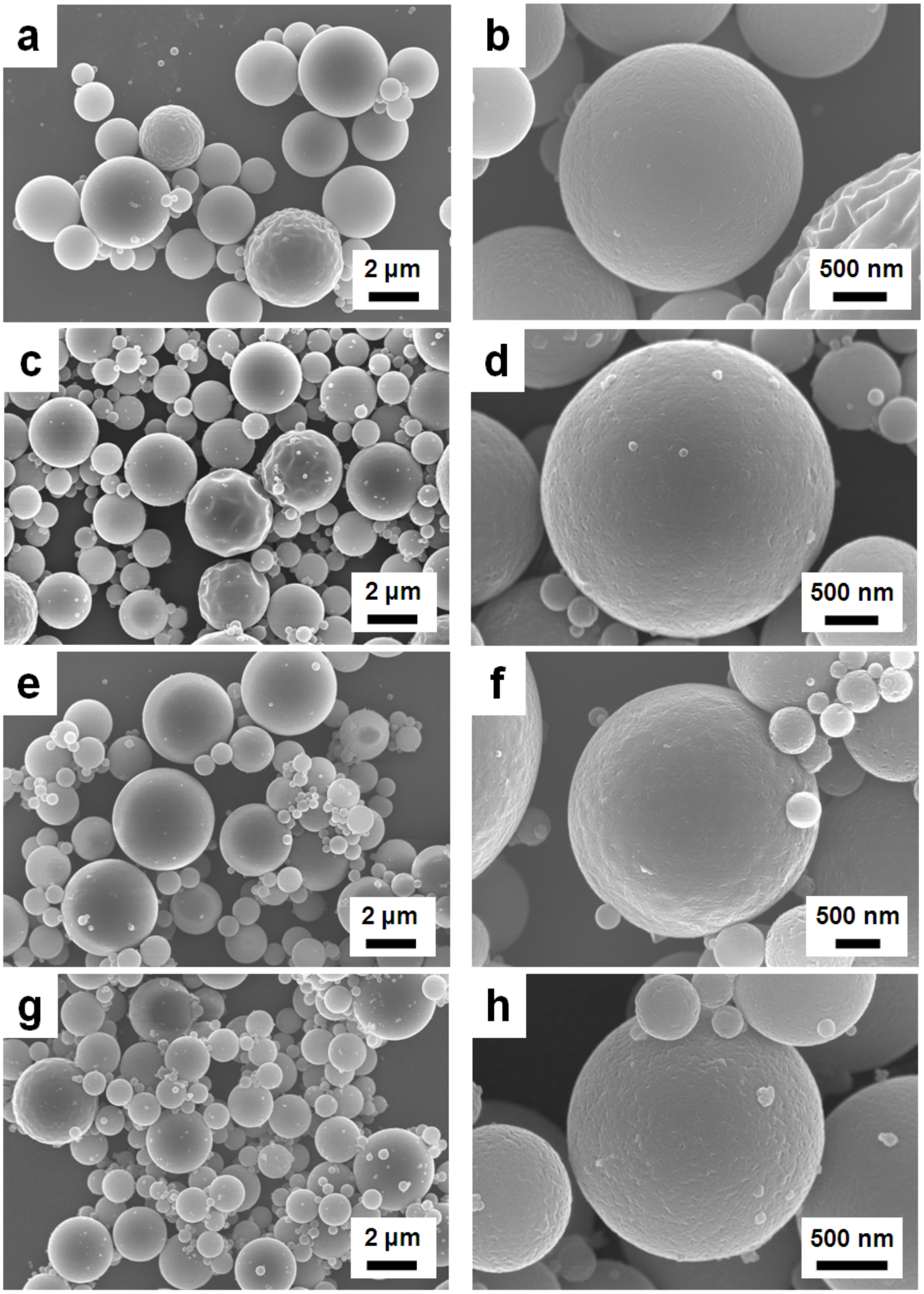

Figure S9. SEM images of a-b) 7N (nickel nitrogen-rich carbon spheres synthesized using the NSP (Nozzle Spray Pyrolysis) at 773 K), c-d) 7NH (Heat treated 7N in H_2 at 673 K), e-f) 6N (nickel nitrogen-rich carbon spheres synthesized using at the NSP at 673 K), and g-h) 6NH (Heat treated 6N in H_2 at 673 K).

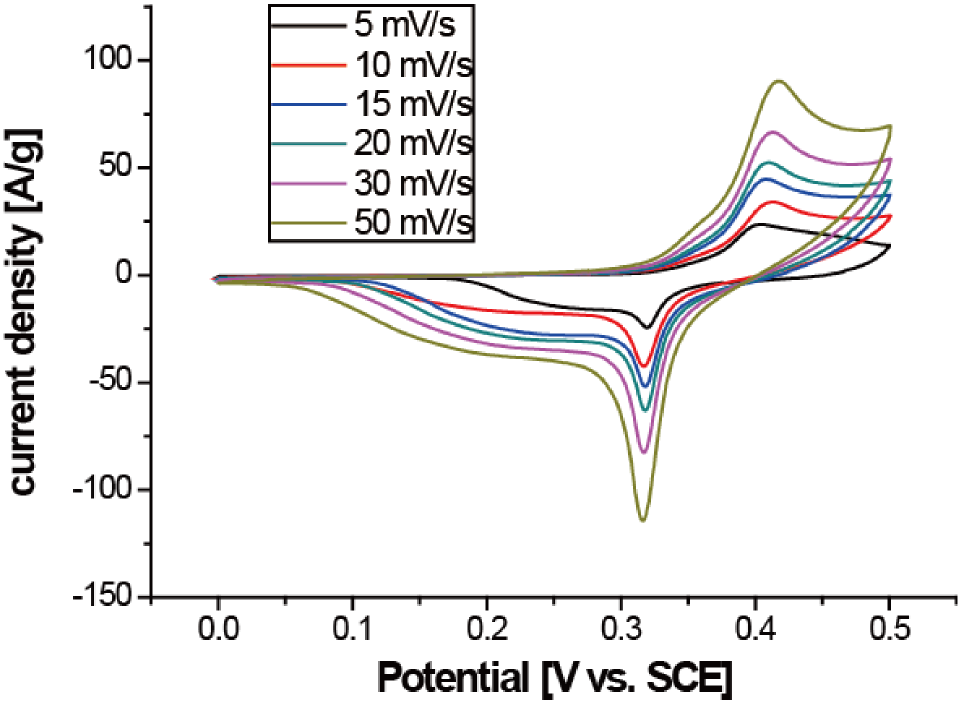

Figure S10. The cyclic voltammetry data of 8NH2 at various scan rates.

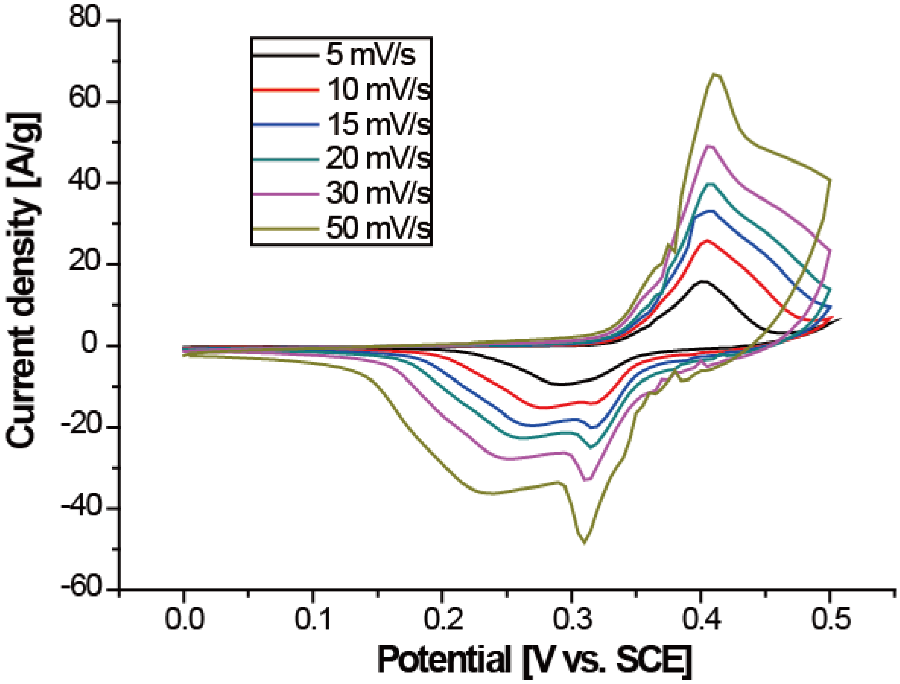

Figure S11. The cyclic voltammetry data of 7NH at various scan rates.

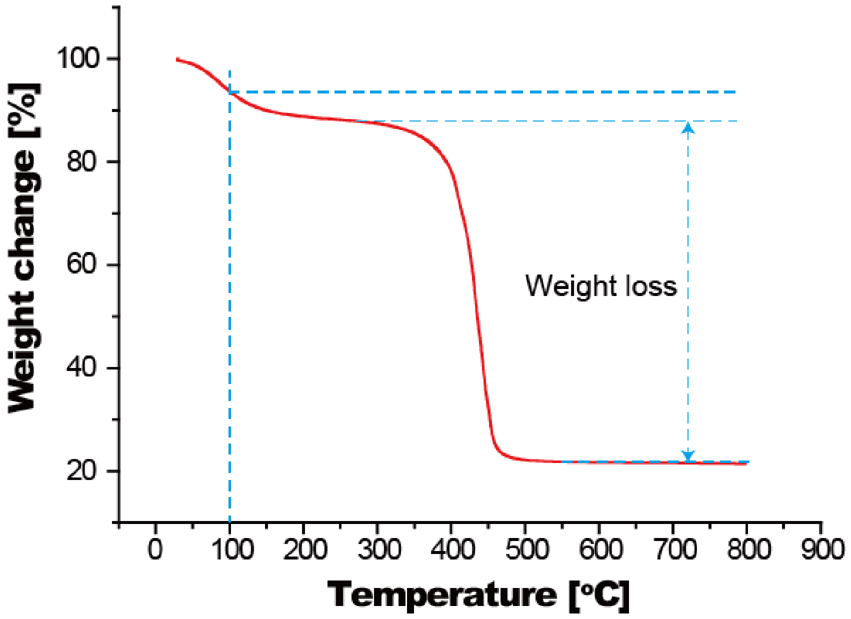

Figure S12 . Thermal gravimetric analysis of 8NH2. The mass portion of the NiO content can be calculated to ~ 24.4 wt. %.

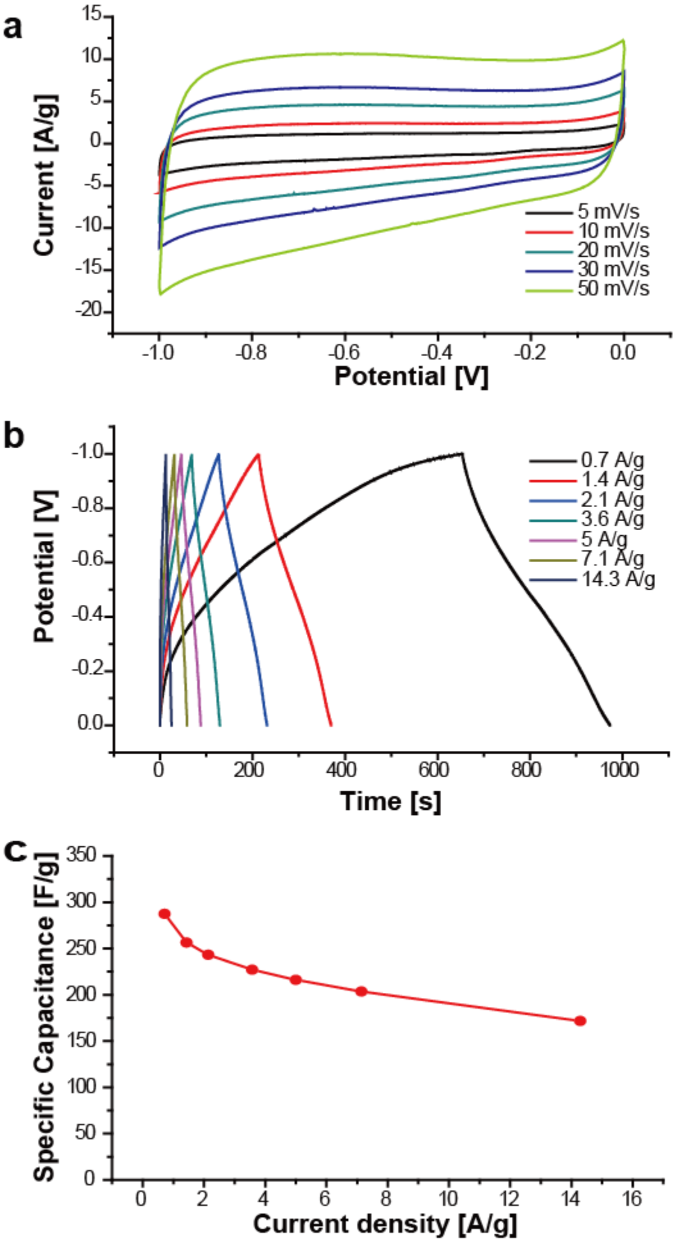

Figure S13. Electrochemical properties of nitrogen-doped graphene (NG) as a negative electrode for an asymmetric supercapacitor. a) CV measurements of NG at various scan rates. b) Charge/discharge profiles measured by galvanostatic characterization at various current densities. c) Gravimetric capacitance of NG measured at a series of current densities.

Table S1. Average and the standard deviation of diameters for nickel nitrogen-rich carbon spheres.

	8N[a)]	8NH1[b)]	8NH2[c)]	7N[d)]	7NH[e)]	6N[f)]	6NH[g)]
Average Diameter (nm)	1047.9	638	644	1171	955	932	743
Standard Deviation of diameters (nm)	829	789	586	971	915	864	686

a) nickel nitrogen-rich carbon spheres synthesized using the NSP (Nozzle Spray Pyrolysis) process at 873 K, b) heat treated 8N in H_2 at 673 K, c) heat treated 8N in N_2 gas flow at 773 K, d) nickel nitrogen-rich carbon spheres synthesized using the NSP process at 773 K, e) heat treated 7N in H_2 at 673 K, f) nickel nitrogen-rich carbon spheres synthesized using the NSP process at 673 K, and g) heat treated 6N in H_2 at 673 K.

Table S2. The elemental ratio of C, N, O, and Ni for nickel nitrogen-rich carbon spheres.

	C	N	O	Ni
6N[a)]	47.84	38.70	9.30	2.61
7N[b)]	58.63	30.08	7.82	1.80
8N[c)]	62.21	25.95	7.58	2.66

Nickel nitrogen-rich carbon spheres synthesized using the NSP process at a) 673 K, b) 773K, and c) 873K.