Electronic supplementary information (ESI) for Journal of Materials Chemistry A

Electronic supplementary information

Synthesis of hollow TiO_2@N-doped carbon with enhanced electrochemical capacitance by *in-situ* hydrothermal process of hexamethylenetetramine†

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Surface characterization of hollow TiO_2·nH_2O@RF polymer, hollow TiO_2 and hollow TiO_2@N-doped carbon: Transmission electron microscope (TEM) images were obtained by an EM912 Omega electron microscope with an acceleration voltage of 120 kV. While high resolution-transmission electron microscope (HR-TEM) images were obtained by using JEM 2200-FS operated at 200 kV, high resolution-scanning electron microscope (HR-SEM) images by using Hitachi S-5500 operated at 30 kV. Powder X-ray diffraction (XRD) patterns of the samples were recorded by employing a Rigaku Smartlab diffractometer with Cu Kα radiation using a Ni β-filter at a scan rate of 0.2 °/min. The X-ray source was operated at 40 kV and 30 mA. Raman spectra were recorded by using Nanofinder®30 (Tokyo Instrument) in Micro-Raman spectrometer. Raman excitation at 488 nm was provided by diode-pumped solid-stage (DPSS) laser. A laser power of 1.011 mW was applied at the sample. X-ray photoelectron spectroscopy (XPS) measurements were obtained with an Escalab 250 XPS system with a monochromated Al Kα line source. Unsupported powder catalyst samples were mounted on carbon tape, and spectra were obtained with 40 eV pass energy, and at a 15 degree take-off angle from the normal surface. Binding energies were referenced to a graphite standard (C 1s = 284.6 eV). Thermogravimetric analyses (TGA) were carried out in air atmosphere using a Bruker TG-DTA3000SA analyzer. Nitrogen adsorption-desorption isotherms were measured at -196 ^oC using a Micromeritics ASAP 2020 system. Specific surface areas of the samples were determined by nitrogen adsorption branch in the relative pressure range from 0.05 to 0.2 using the Brunauer-Emmett-Teller (BET) equation. Total pore volumes were determined from the amount of gas adsorbed at the relative pressure of 0.99. Pore size distribution (PSD) was calculated from adsorption branch by the Barrett-Joyner-Halenda (BJH) method.

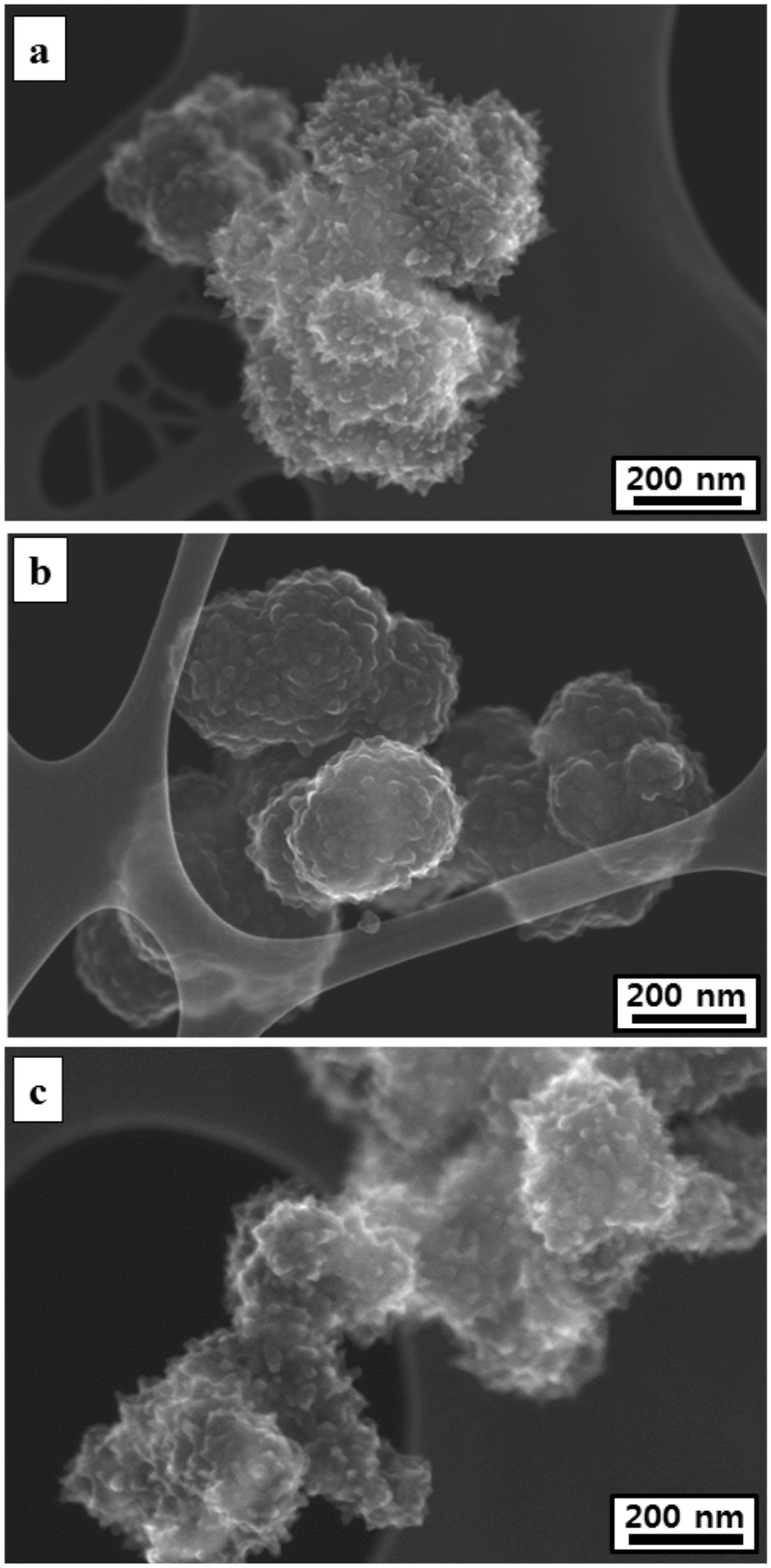

Fig. S1 Representative HR-SEM images for (a) hollow $TiO_2 \cdot nH_2O$@RF polymer, (b) hollow TiO_2 and (c) hollow TiO_2@N-doped carbon.

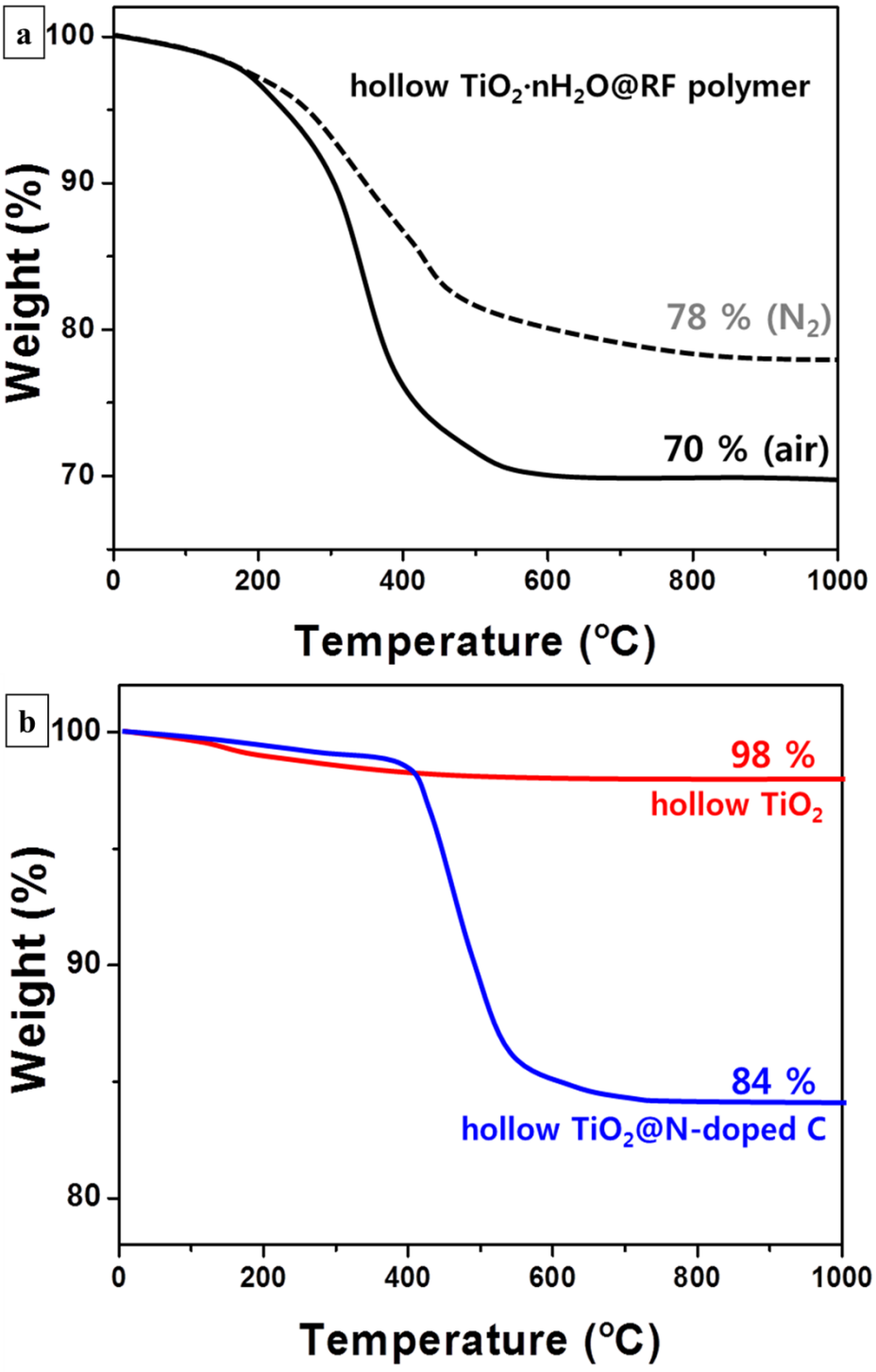

Fig. S2 TGA profiles showing the change in weight as a function of calcination temperature for (a) hollow $TiO_2 \cdot nH_2O$@RF polymer with a heating rate of 5 °C/min under air and N_2 atmosphere, and (b) hollow TiO_2 and hollow TiO_2@N-doped carbon prepared at 600 °C with a heating rate of 5 °C/min under air.

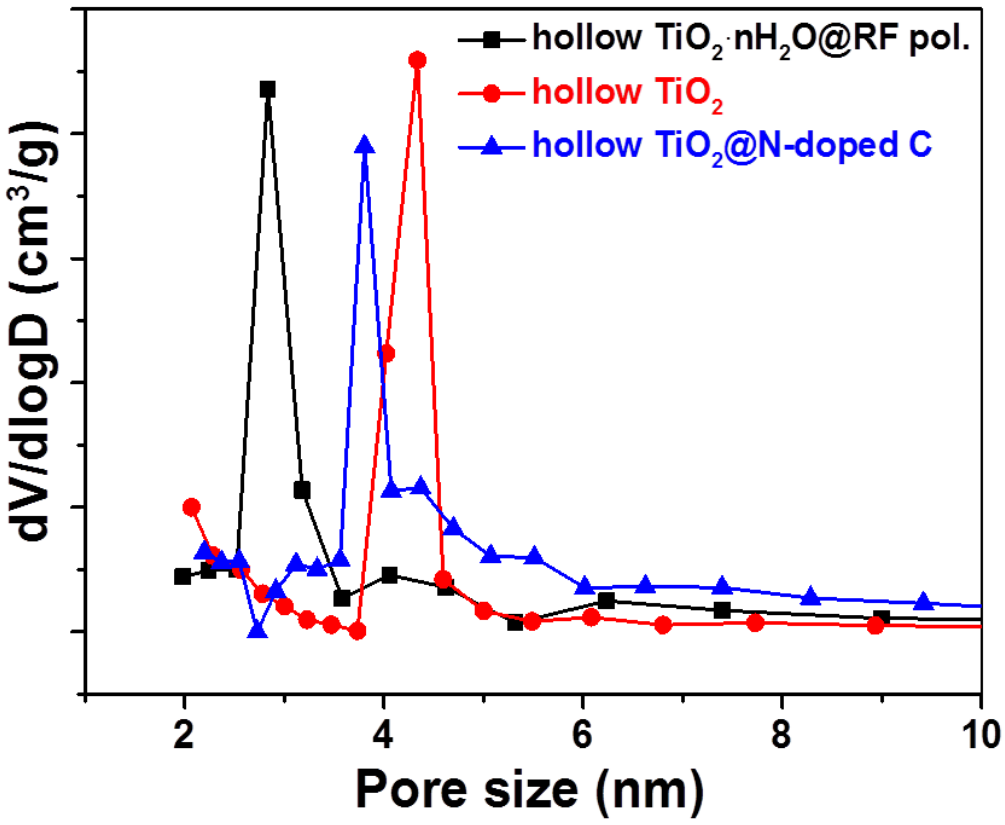

Fig. S3 The pore size distribution curves for hollow $TiO_2 \cdot nH_2O$@RF polymer, TiO_2 and TiO_2@N-doped carbon samples.

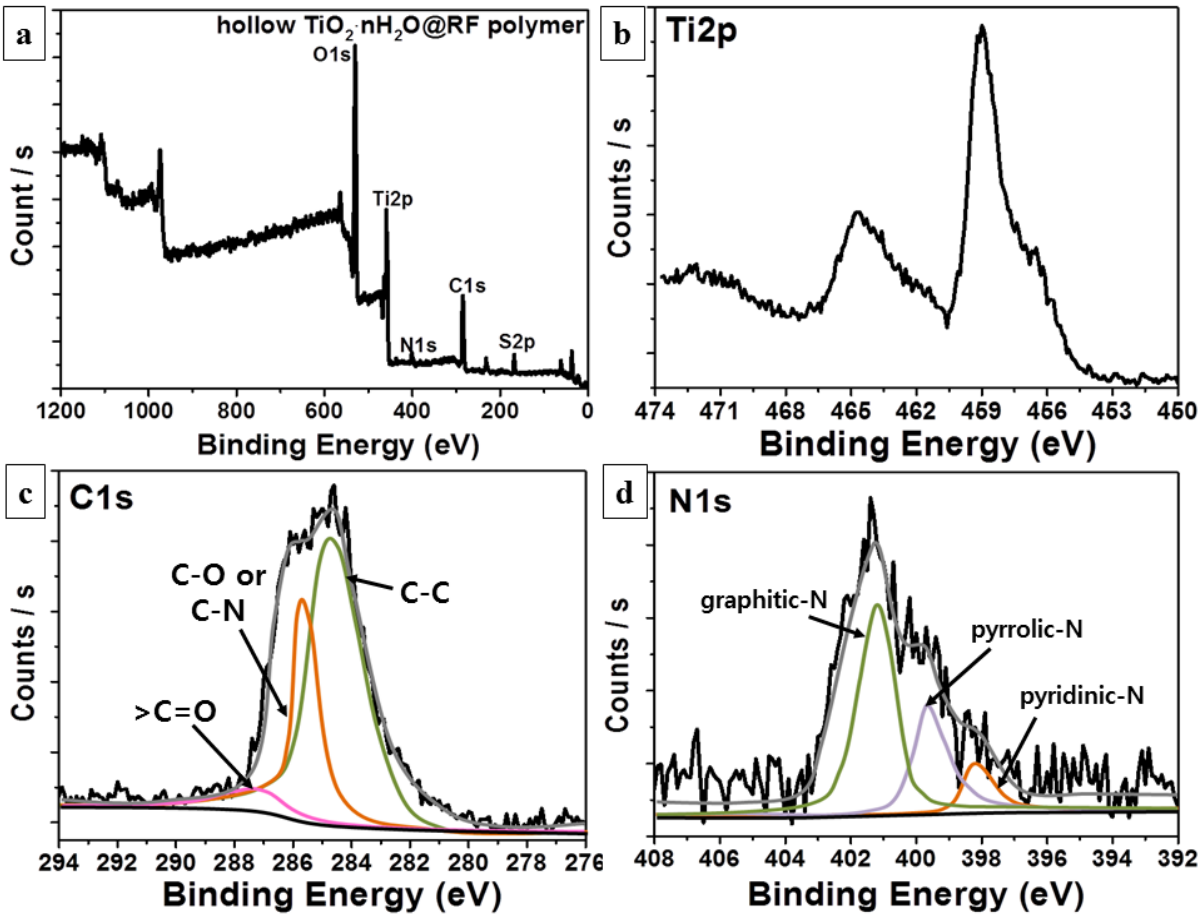

Fig. S4 XPS survey scan (a) for hollow $TiO_2 \cdot nH_2O$@RF polymer and corresponding narrow range XPS spectra and deconvoluted curves for (b) Ti 2p, (c) C 1s and (d) N 1s.

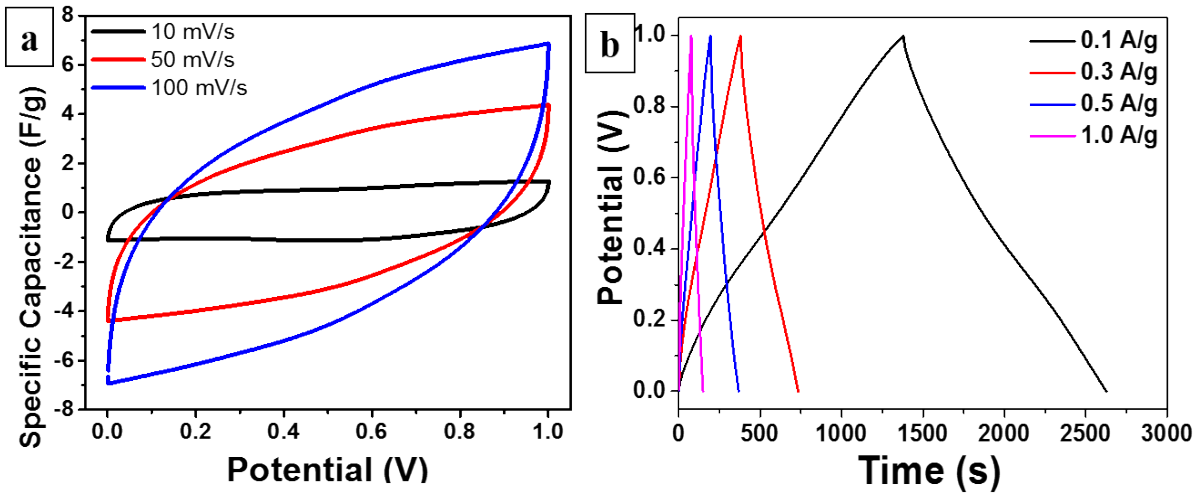

Fig. S5 (a) Cyclic voltammetry curves at scan rates of 10, 50, and 100 mV/s, and (b) galvanostatic charge-discharge curve at current densities of 0.1, 0.3, 0.5, and 1.0 A/g of hollow TiO_2@N-doped carbon.

Table S1. Nominal composition of $TiO_2 \cdot nH_2O$@RF polymer, hollow TiO_2 and TiO_2@N-doped carbon prepared at 600 °C determined by XPS spectra.

Element	hollow $TiO_2 \cdot nH_2O$@RF polymer		hollow TiO_2		hollow TiO_2@N-doped carbon	
	at.%	wt. %	at.%	wt. %	at.%	wt. %
C	33.68	21.33	9.72	5.02	44.50	28.44
N	3.68	2.72	1.68	1.01	2.18	1.62
O	47.18	39.81	64.40	44.25	38.90	33.12
Ti	11.97	30.22	24.20	49.72	14.42	36.82
S	3.50	5.92	-	-	-	-

Table S2. Summary of fitted impedance parameters of hollow TiO_2 and hollow TiO_2@N-doped carbon.

Sample	Solution resistence (R_s) Ω	Charge transfer resistence (R_{ct}) Ω	Warburg impedence (Z_W) Ω. $sec^{-1/2}$	Capaciatnce (C) mF
hollow TiO_2	4.92	3.04	84.29	200
hollow TiO_2@N-doped carbon	2.95	1.81	81.95	280