Supporting Information for:

High surface area ceramic-derived-Boron-nitride and its hydrogen uptake properties

TiB₂ (Aldrich) and TiN (Aldrich) powders were mixed by high energy ball milling. Since this process is conducted by direct surface reaction, the extent of mixing significantly affects the quantity of product. For the least contamination, YSZ ball and zirconia jar were used at 200rpm for 20h. The experimental procedure was followed by usual CDC experiment.¹ The starting material (2g; TiB₂: TiN=1:2 molar ratio for the BN stoichiometry) was placed in the quartz boat and injected into the quartz tube of the furnace. Then the furnace is heated to the desired temperature (500~800°C) under argon purge. When the temperature was reached, chlorination was performed under chlorine with a

10sccm for 3h. To remove unreactive or chemically adsorbed chlorine trapped in pore, hydrogen annealing was also performed at 600°C for 2h. Assumed that Titanium and Chlorine is fully removed (According to XPS analysis, it seems reasonable except BN-500), the product yield was around 60~65%. XRD diffraction patterns were analyzed by M18XHF-SRA (Macscience, Japan) using Cu-Ka. XPS (X-ray Photoelectron Spectroscopy) was performed using AXIS-NOVA (Kratos. Inc., UK) with monochromatic Al-K α at the 3.0*10⁻⁹ Torr (Figure S1). Elemental analysis was also done by XPS instrument to confirm the residues like titanium and chlorine (Table S1). Field-emission scanning electron microscope (FE-SEM) instrument, JSM-6330F (JEOL), was used for morphology analysis and depicted in Figure S2. N₂ adsorption was measured at 77K on a BELSORP-mini II (BEL Japan Inc., Japan) after degassing under vacuum at 300°C for 20h. Specific surface area was estimated by BET (Brunauer-Emmett-Teller) equation with the 0.01-0.10 relative pressure range. 0.6~0.7nm size pore, optimum size for hydrogen storage², were well developed in BN-600, BN-700, and BN-800 as shown in Figure S3 (MP-plot method). Low pressure H₂ uptake was also measured by BELSORP-mini II (BEL Japan Inc., Japan) after degassing under vacuum at 300°C for 20h with 77K, 87K both (Figure S4).



Figure S1. XPS (X-ray Photoelectron Spectroscopy) spectrum of B and N 1s

for BN-600, respectively.

	BN-500	BN-600	BN-700	BN-800
Ti amount (wt%)	0	0	0	0
Cl amount (wt%)	5.6	0.8	0.7	0.7

Table S1. Residual amounts of titanium and chlorine in BN series measured by XPS.



Figure S2. FE-SEM images of BN series (scale bars: 1µm).



Figure S3. Micropore size distribution of BN series based on MP-plot method.



Figure S4. Low-pressure hydrogen uptake properties of BN series at 77K. Closed symbols for adsorption and open symbols for desorption.

The dependence of the isosteric heat of adsorption (Q_{st}) on the surface coverage level (θ) was estimated using the Clausius–Clapeyron equation as follows.

$$Q_{st} = -R[\frac{\partial \ln(P)}{\partial (1/T)}]_{\theta}$$

Where R means the gas constant, P the pressure and T the temperature. From the plotted line of ln(P) vs. 1/T(T for 77K, 87K), we can get the slope of the line used to get the Q_{st} at each pressure point.

Langmuir-Fruendlich fit for the isotherms was used to determine Pressure as a function of the amount of H_2 adsorbed.³

 $\frac{M}{M_{max}} = \frac{A \times P^{(\frac{1}{t})}}{1 + A \times P^{(\frac{1}{t})}}$ (M: moles absorbed, M_{max}: moles adsorbed at saturation, P:

pressure, A: constant, t: constant)

Determined values of BN-600 based on these equations are listed in this table S2.

H ₂ uptake		H ₂ uptake	
2	Q _{st} (kJ/mol)		Q _{st} (kJ/mol)
(wt%)		(wt%)	
0.01	12.0998	0.32	7.33183
0.02	11.06989	0.33	7.30359
0.03	10.47221	0.34	7.27703
0.04	10.05161	0.35	7.25207
0.05	9.7281	0.36	7.22866
0.06	9.46608	0.37	7.20672
0.07	9.24655	0.38	7.18621
0.08	9.05816	0.39	7.16707
0.09	8.89361	0.4	7.14926
0.1	8.7479	0.41	7.13274
0.11	8.61748	0.42	7.11746
0.12	8.49971	0.43	7.10341
0.13	8.39261	0.44	7.09054
0.14	8.29462	0.45	7.07883
0.15	8.20452	0.46	7.06825
0.16	8.12131	0.47	7.05879
0.17	8.0442	0.48	7.05041
0.18	7.97251	0.49	7.0431
0.19	7.90568	0.5	7.03685
0.2	7.84324	0.51	7.03164
0.21	7.78479	0.52	7.02746

0.22	7.72999	0.53	7.0243
0.23	7.67853	0.54	7.02215
0.24	7.63015	0.55	7.02099
0.25	7.58463	0.56	7.02083
0.26	7.54178	0.57	7.02166
0.27	7.5014	0.58	7.02348
0.28	7.46335	0.59	7.02628
0.29	7.42748	0.6	7.03007
0.3	7.39368	0.61	7.03484
0.31	7.36183	0.62	7.04059
		0.63	7.04733

Table S2. Estimated values of the heat of the adsorption (Q_{st}) about BN-600 according to H_2 uptake based on Clausius-clapeyron equation and Langmuir-freundlich fitting.

- 1. V. Presser, M. Heon and Y. Gogotsi, *Adv. Funct. Mater.*, 2011, **21**, 810-833.
- Y. Gogotsi, R. K. Dash, G. Yushin, T. Yildirim, G. Laudisio and J. E. Fischer, J. Am. Chem. Soc., 2005, 127, 16006-16007.
- 3. J. An, S. J. Geib and N. L. Rosi, J. Am. Chem. Soc., 2010, 132, 38-39.