Supplementary Information for

Cyclopentadienyl Chromium Hydrazide Gels for Kubas-Type Hydrogen Storage

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Extended Experimental

Synthesis of Cyclopentadienyl Chromium Hydrazide Materials

1 CrN21 materials. Bis cyclopentadienyl chromium (4g, 22mmol), purchased from Strem Chemicals, was mixed with 100ml toluene and stirred at 50°C for 60 minutes under argon until a homogeneous solution was obtained. Anhydrous hydrazine (0.37ml, 11mmol), dried and distilled using a toluene azeotrope, was added dropwise to the solution. The reaction vessel was sealed and the stirred at 50°C for 4hours, 75°C for 4 hours, and 100°C for 24 hours. The precipitate was collected by filtration and dried under vacuum at room temperature for 6 hours, and the collected black solid was then heated *in vacuo* at 0.02mmHg and 60^{0}Cfor 48 hours to yield CrN2160, 100°C for 48 hours to yield CrN21100, and 150°C for 48 hours to yield CrN21150. Materials were synthesized 4

times at each set of conditions in order to guarantee reproducible hydrogen storage results for each composition.

2 CrN11 materials. The materials CrN1160, CrN11100, and CrN11150 were made by the same procedure described above for the CrN21 materials, however a molar ratio of 1 : 1 between bis cyclopentadienyl chromium and hydrazine was used.

3 CrN12 materials. The materials CrN1160, CrN11100, and CrN11150 were made by the same procedure described above for the CrN21 materials, however a molar ratio of 1 : 2 between bis cyclopentadienyl chromium and hydrazine was used.

Elemental analysis for these materials is provided in table S7.

Ratio BisCpCr/N_2H_4	Heating at 60°C	Heating at 100°C	Heating at 150°C
2 : 1	CrN2160	CrN21100	CrN21150
1 : 1	CrN1160	CrN11100	CrN11150
1 : 2	CrN1260	CrN12100	CrN12150

Table S1. Sample names for cyclopentadienyl chromium Hydrazide Gels

*All reactions were conducted in an argon glove box using rigorously moisture and air-free conditions.

Hydrogen adsorption measurements

The hydrogen adsorption/desorption isotherms were measured by a computer controlled commercial Sieverts apparatus manufactured by Advanced Materials Corporation, Pittsburgh, PA. Highly purified hydrogen (99.9995% purity) was used as the adsorbent. Typically the mass used for the hydrogen sorption measurement was 500-1000mg. The size of the sample chamber is 2.5 cm^3. Lightly packed powder materials were used for all measurements. Before all measurements the materials were degassed at 200^{o}C under high vacuum for at least one day in order to remove any volatile impurities. A simplified sketch of this apparatus is shown in Figure S1. The temperature of the gas reservoir is measured by two AD590 IC thermometers that are calibrated against a standard mercury thermometer within 0.1^{o}C at room temperature. The sample temperature is measured with type K thermocouple by converting a voltage reading to temperature according to ITS-90 (The International Temperature Scale of 1990). The limits of error are 2^{o}C or 0.75 % above 0^{o}C and 2^{o}C or 2 % below 0^{o}C. The pressure of both the gas reservoir and sample chamber is measured by Heise model HP0 pressure transducer, which has a range of 1500 psi (about 100 bar). The accuracy of this transducer is rated to be 0.05 % of the full scale including non-linearity, drift, and hysteresis. The GRC operates by admitting an appropriate amount of gas to the reservoir and determines its molar amount from its pressure and temperature. The system then manipulates the valves between the reservoir and the reaction chamber and transfers a desired amount of the gas from the reservoir to the gas reaction chamber. After equilibrium is attained, the system re-calculates the number of hydrogen molecules. The number missing from the gas phase corresponds to the number of molecules absorbed by the sample. The system employs a modified Benedict-Webb-Rubin equation of state in calculating the amount of absorbed hydrogen from the pressure, temperature, and volume. The apparatus gradually increases the hydrogen pressure to the maximum specified value, while summing the sorbed hydrogen. The amount of hydrogen released from the sample is then determined by pumping out the gas reservoir and gradually bleeding hydrogen from the sample chamber into the gas reservoir. During the test process the sample chamber was immersed in water for room temperature measurements and liquid nitrogen or liquid argon for cryogenic measurements, and the liquid level was maintained unchanged.

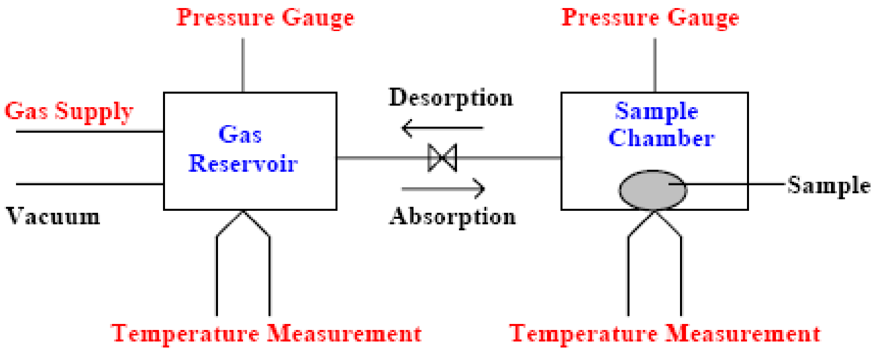

Figure S2. Schematic drawing of the GRC system

The isosteric heats of adsorption (ΔH) were calculated using hydrogen-adsorption isotherms measured at different temperatures (77K and 87K) based on the Clausius–Clapeyron equation.

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{ads} * \frac{T_2 - T_1}{R * T_1 * T_2}$$

Where

P_i : Pressure for isotherm i

T_i : Temperature for the isotherm i

R: Gas constant

Pressure as the function of the amount adsorbed was determined by using exponential fit for each isotherm, the first ten points of the isotherms were picked and fit to the exponential equation (See figures S13a-S13c). This exponential equation gives an accurate fit over the pressure up to 10 bar and with the goodness of fit (R^2) above 0.97. The corresponding P_1 and P_2 at a certain amount H_2 adsorbed of both temperatures can be obtained by the simulated exponential equation. Then input these numbers into the equation 1, the enthalpies of the adsorption were calculated.

Characterization

Powder X-ray diffraction (XRD) was performed on Siemens D-500 diffractometer with Cu Kα radiation (40KV, 40mA). The step size was 0.02° and the counting time was 0.3s for each step. Diffraction patterns were recorded in the 2θ range 2.3 - 30°. Samples for XRD analysis were put in a sealed capillary glass tube to protect sample from air and moisture during experiment.

Nitrogen adsorption and desorption data were collected on a Micromeritics ASAP 2010

The skeletal densities of the samples were measured by a Quantachrome Micro-Ultrapycnometer 1000 using helium gas.

XPS (X-ray photoelectron spectroscopy) measurements were performed at Hydro-Québec Research Institute, Chemistry and Materials, 1800 Boul. Lionel-Boulet, Varennes, Quebec, J3X 1S1, Canada. All emissions were referenced to the carbon C 1s (CF_2) peak of a Teflon internal standard at 292.3 eV using a Physical Electronics PHI-5500 spectrometer. Charge neutralization was not necessary.

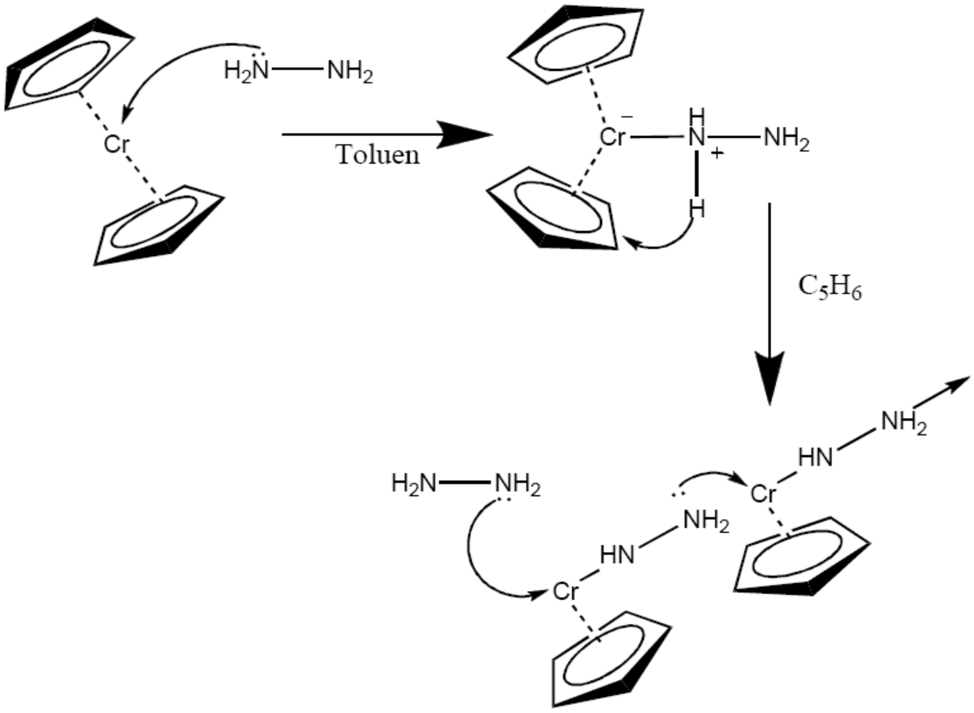

Figure S3. Proposal mechanism of reaction between bis cyclopentadienyl chromium with hydrazine

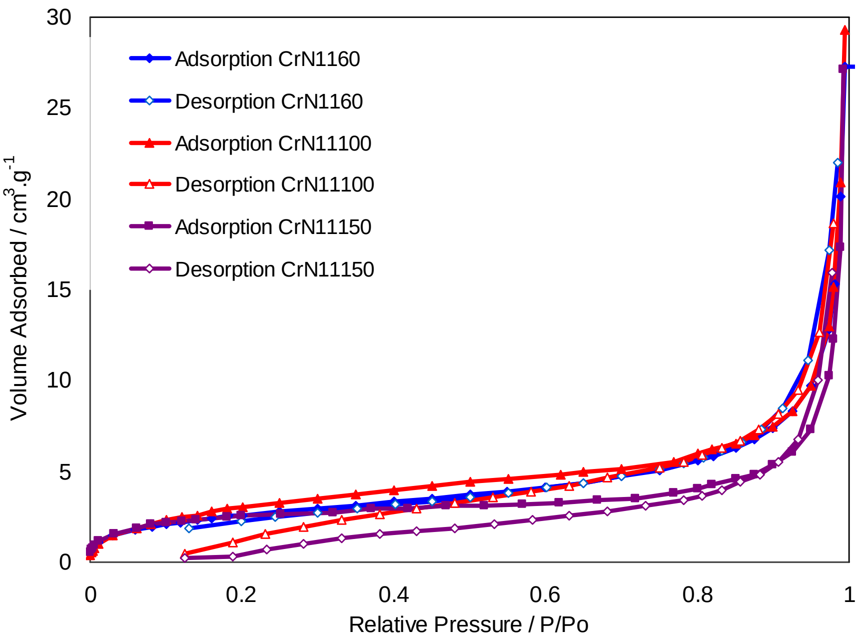

Figure S4a. Nitrogen adsoprtion/desorption isotherm of CrN11 materials.

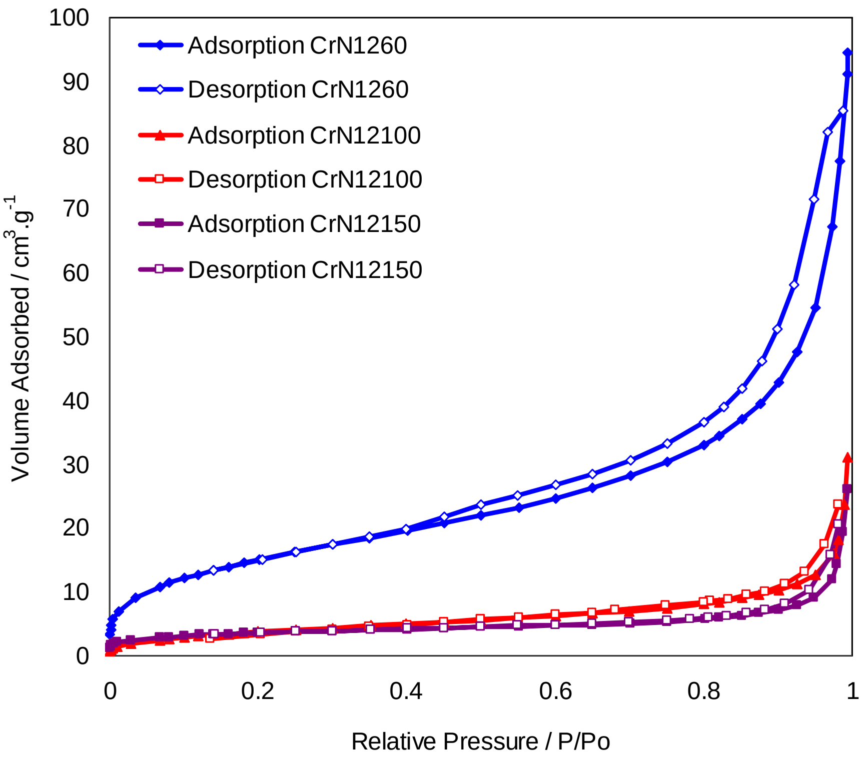

Figure S4b. Nitrogen adsoprtion/desorption isotherm of CrN12 materials.

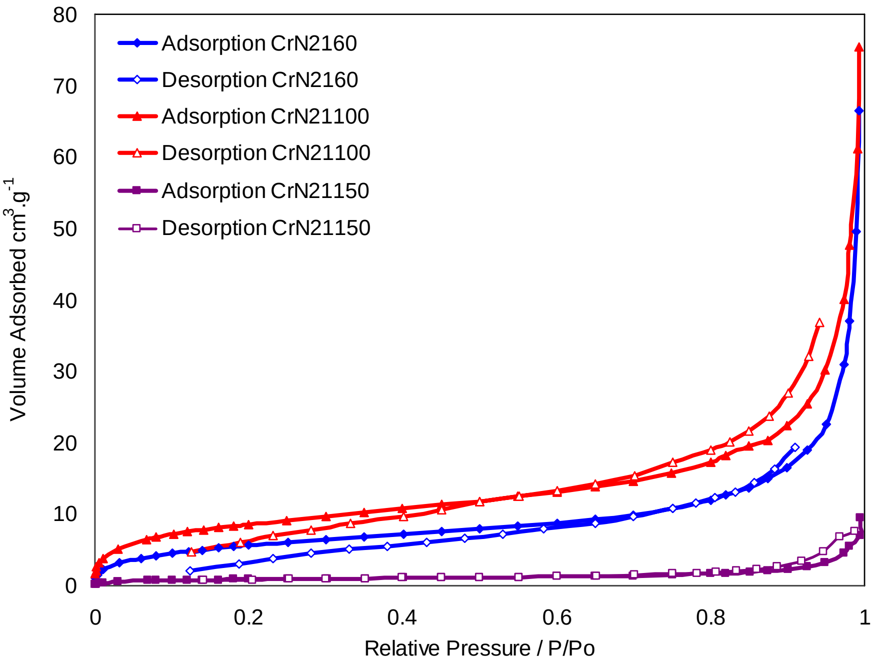

Figure S4c. Nitrogen adsoprtion/desorption isotherm of CrN21 materials.

Sample name	B.E.T. Surface Area (m^2/g)	Skeletal Density (g/cm^3)	Gravimetric Adsorption (wt%) at 77K, 80 bar	Volumetric Adsorption (Kg/m^3) at 77K, 80 bar	Gravimetric Adsorption (wt%) at 87K, 80 bar	Volumetric Adsorption (Kg/m^3) at 87K, 80 bar	Gravimetric Adsorption (wt%) at 298K, 80 bar	Volumetric Adsorption (Kg/m^3) at 298K,80 bar
CrN2160	21.58	1.591	0.93	14.80	NA	NA	0.23	3.66
CrN21100	32.07	1.313	1.56	20.48	NA	NA	0.45	5.91
CrN21150	19.06	2.247	1.41	31.68	NA	NA	0.36	8.09
CrN1160	9.85	1.583	0.78	12.35	0.56	8.86	0.21	3.32
CrN11100	12.08	1.613	1.75	28.23	1.34	21.61	0.73	11.77
CrN11150	9.40	1.433	1.47	21.06	1.01	14.47	0.44	6.30
CrN1260	26.67	1.937	0.86	18.36	NA	NA	0.11	2.13
CrN12100	14.88	1.782	1.23	21.92	NA	NA	0.34	6.06
CrN12150	13.10	2.135	1.06	22.63	NA	NA	0.27	5.76

Table S5. Hydrogen adsorption capacity and surface areas of cyclopentadienyl chromium hydrazide materials

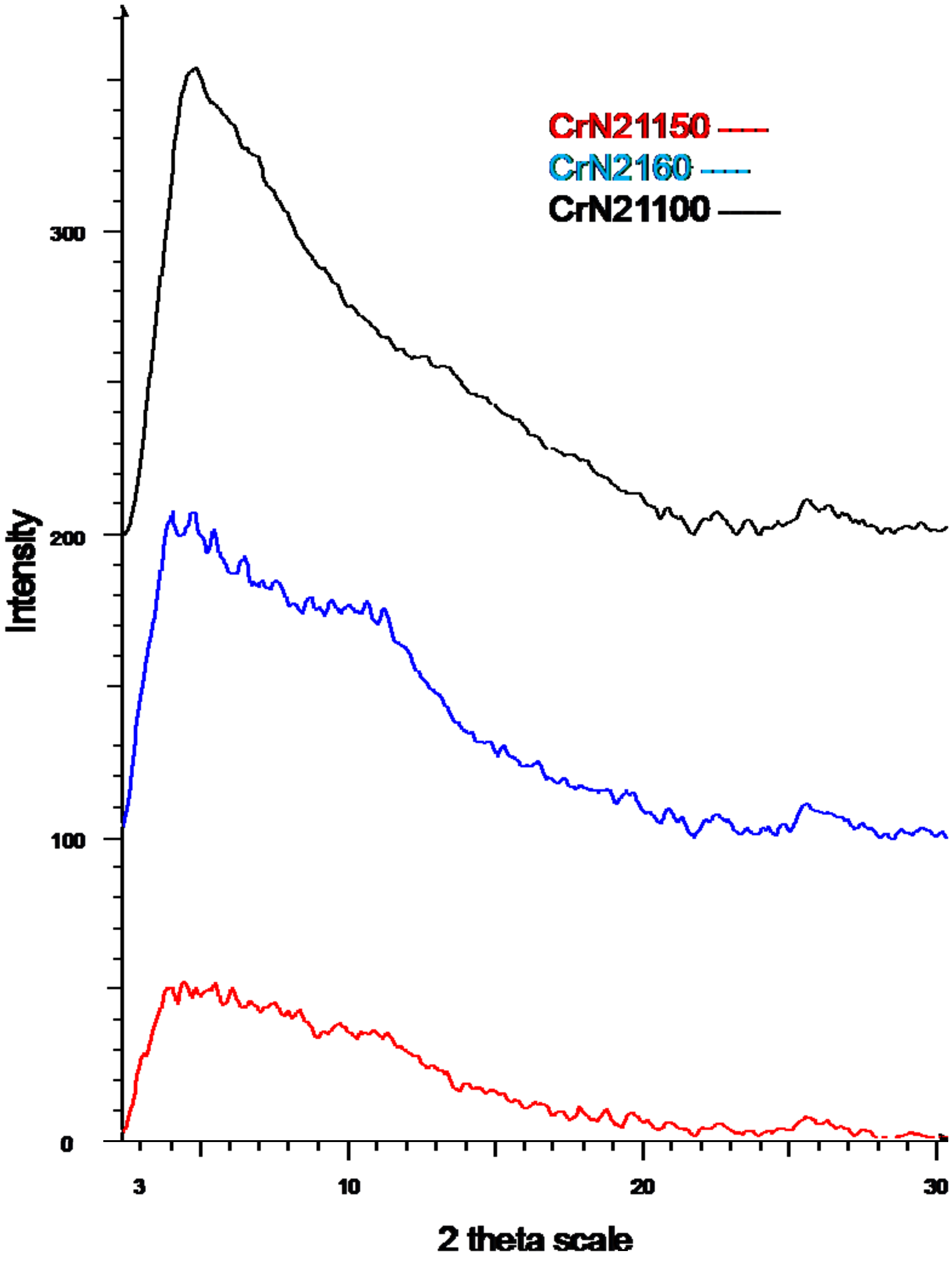

Figure S6b. XRD powder patterns of CrN21.

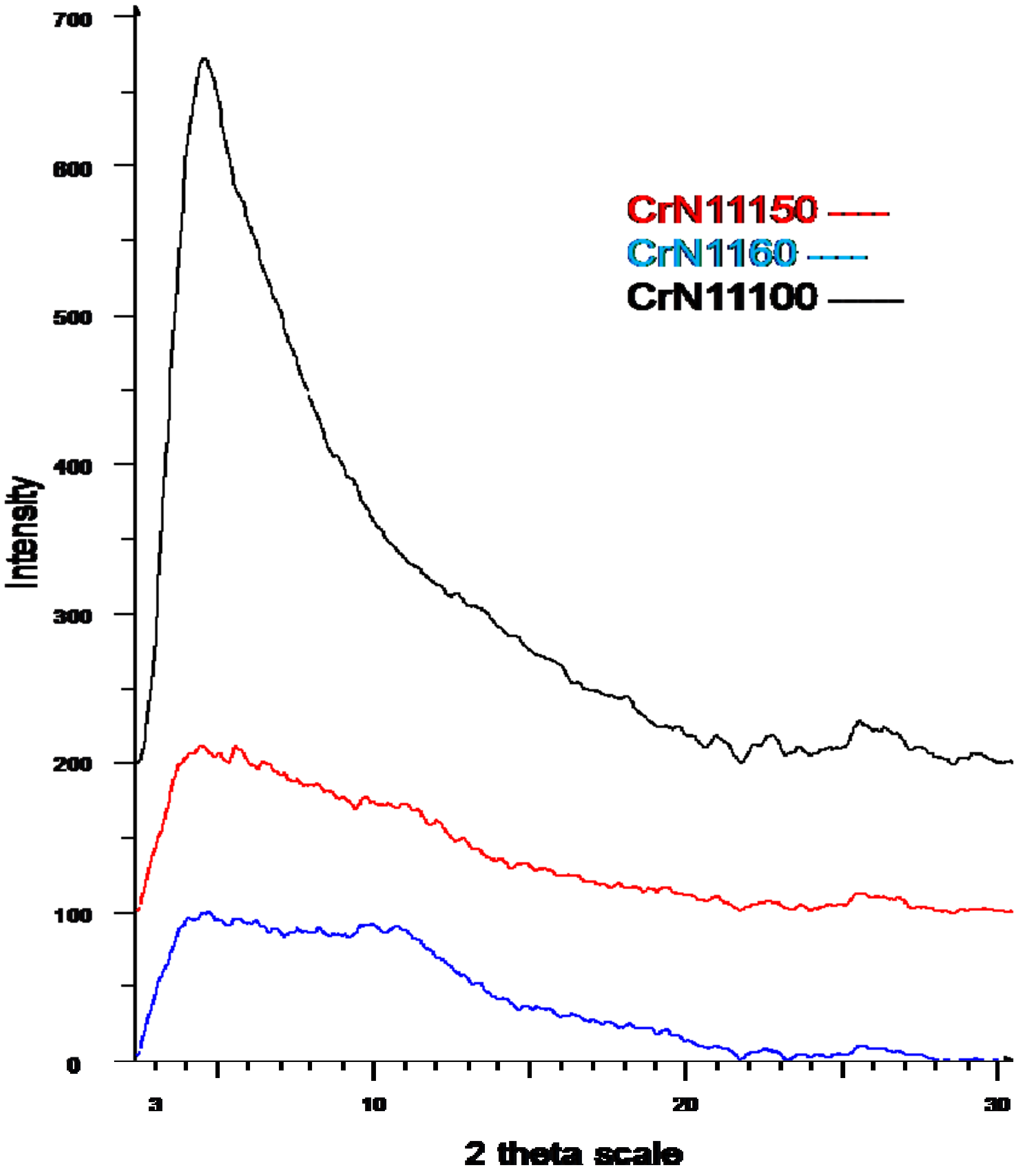

Figure S6a. XRD powder patterns of CrN11 materials.

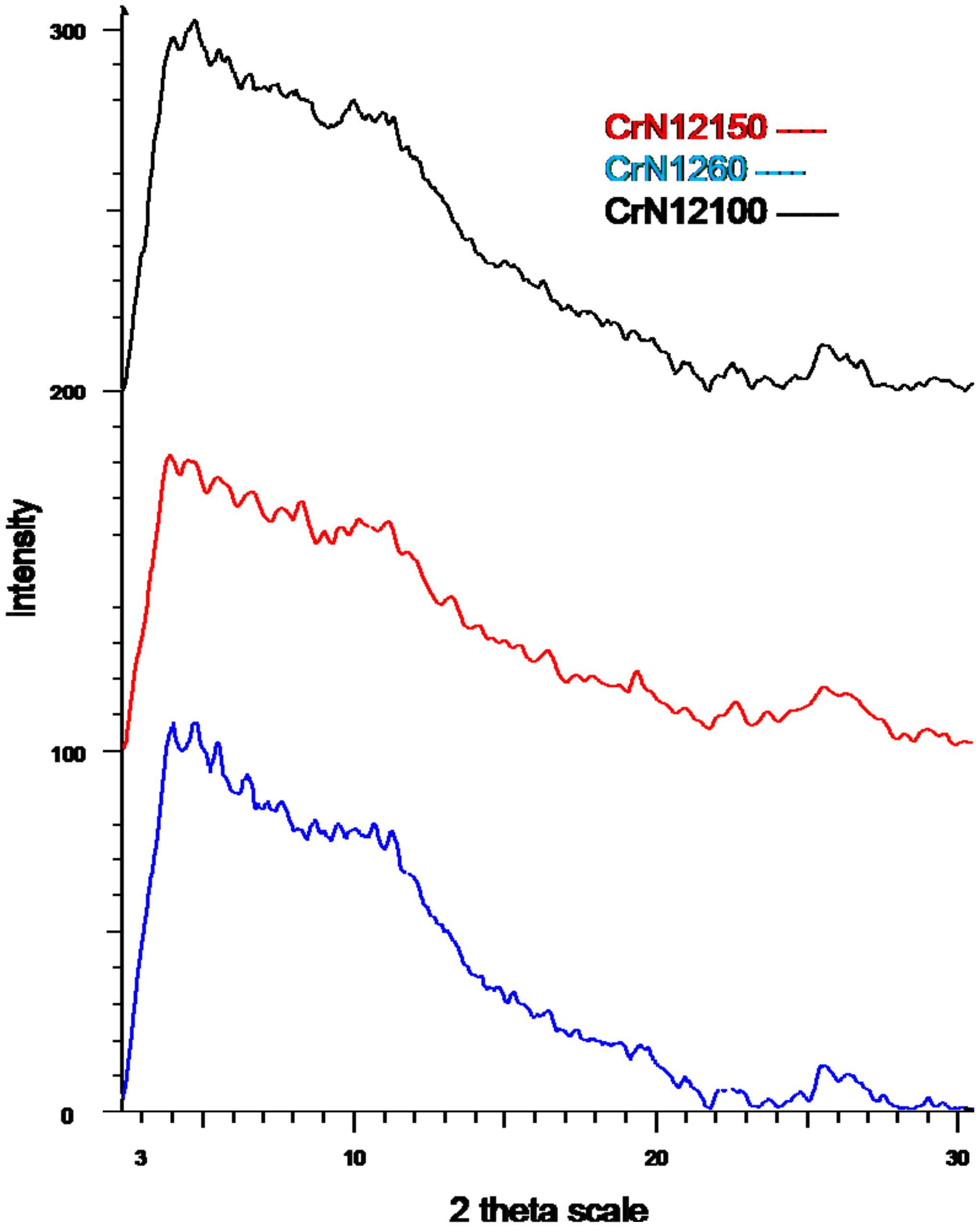

Figure S6c. XRD powder patterns of CrN12 materials.

Material	C%	Cr%	H%	N%
CrN2160	23.83	32.75	4.54	12.48
CrN21100	7.82	42.30	3.01	3.80
CrN21150	10.17	42.80	2.06	3.30
CrN1160	13.86	40.25	2.80	6.05
CrN11100	12.36	46.75	2.52	6.86
CrN11150	8.90	47.80	1.98	3.88
CrN1260	10.59	44.75	3.14	9.32
CrN12100	11.60	43.60	2.85	8.46
CrN12150	8.53	50.90	1.60	3.38
$(C_5H_8N_2Cr)_n$	40.81	35.37	4.76	19.04

Table S7. Elemental analysis of Cyclopentadienyl Chromium Hydrazide materials

*Elemental analysis was measured by Galbraith Laboratories, Inc. 2323, Sycamore Drive, Knoxville, TN 37921.

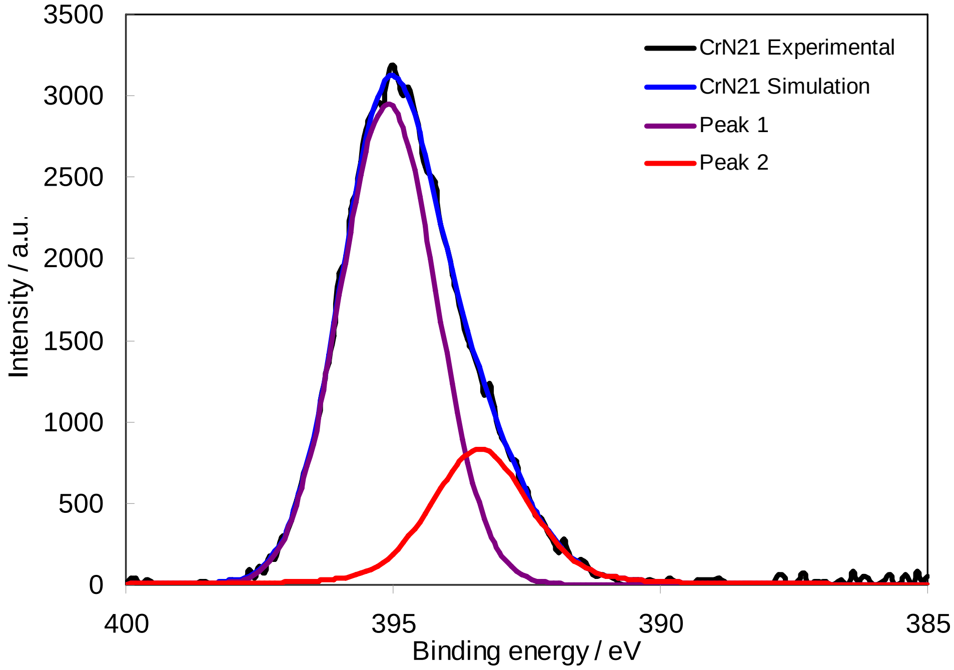

Figure S8a. N 1s region of the XPS spectrum of CrN21100.

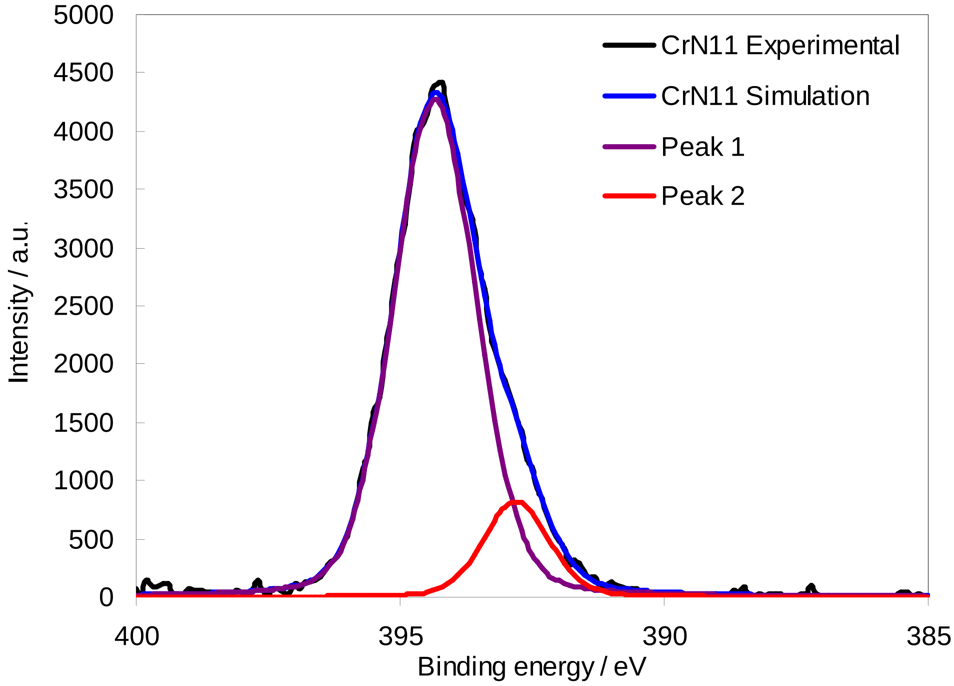

Figure S8b. N 1s region of the XPS spectrum of CrN11100.

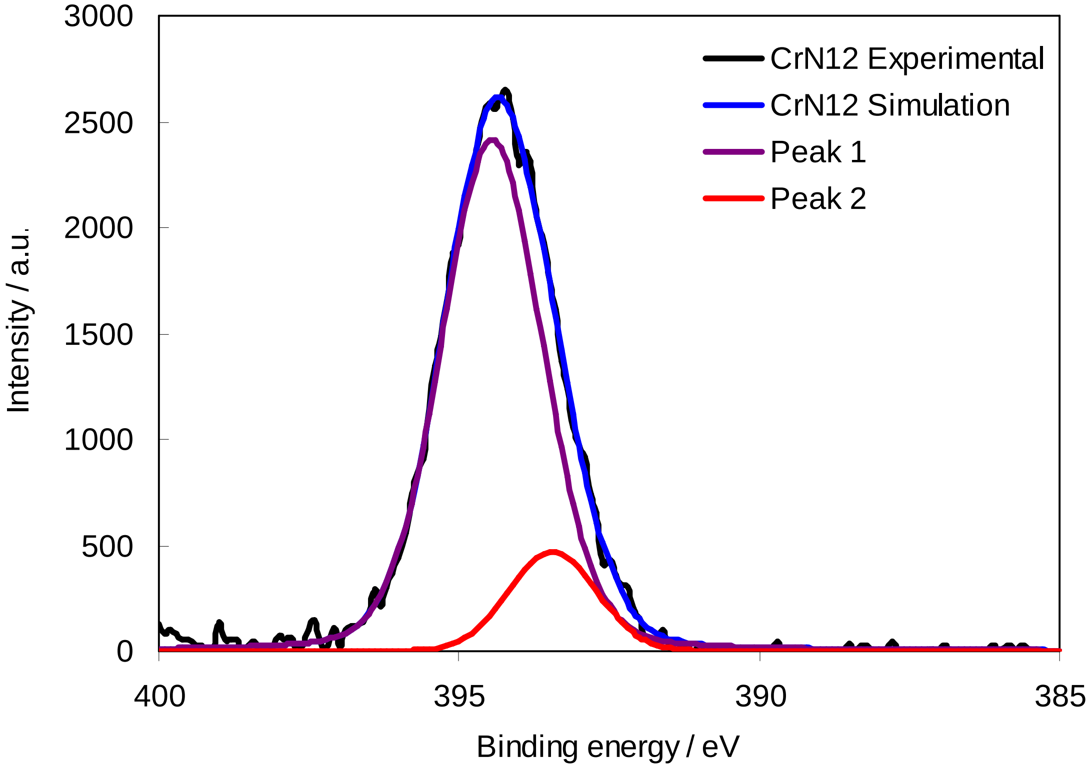

Figure S8c. N 1s region of the XPS spectrum of CrN12100.

* Data were collected in the sequence of a survey scan (to determine the C 1s reference) followed by scans of the C 1s, N 1s, Cr 2p, and O 1s regions to minimize the time of exposure to X-rays.

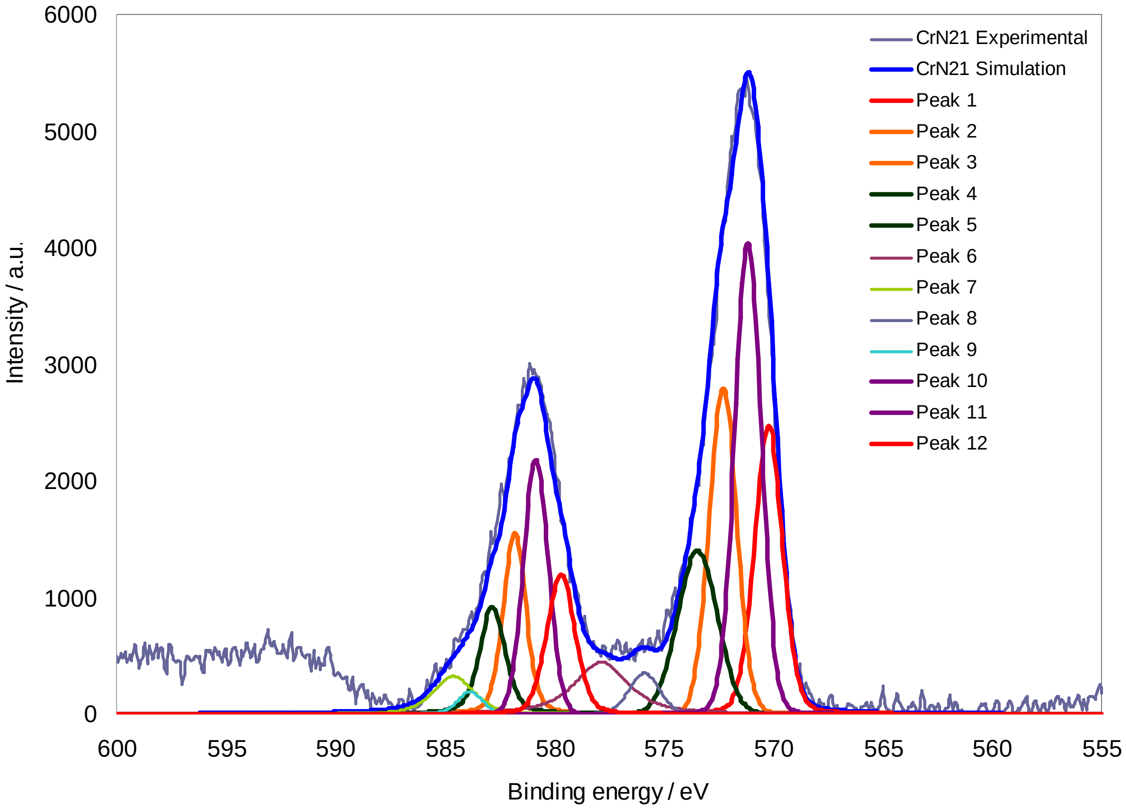

Figure S9a. Cr 2p region of the XPS spectrum of CrN21100.

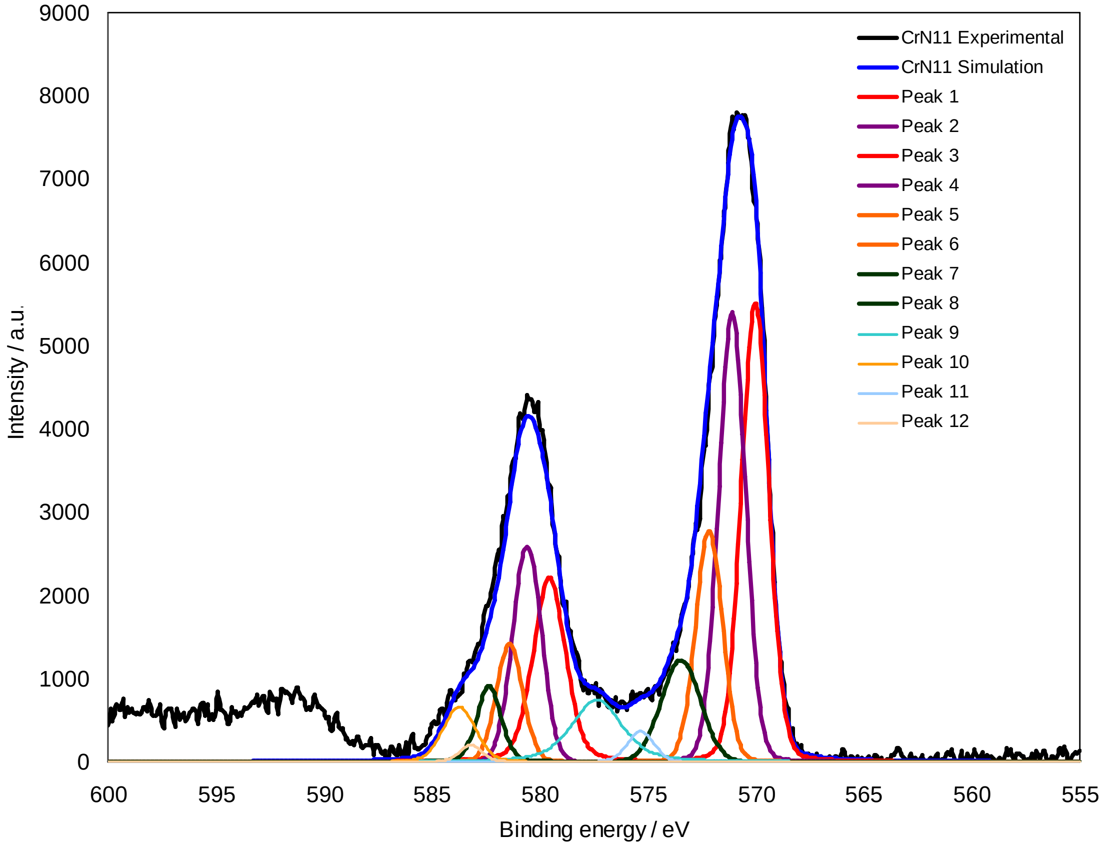

Figure S9b. Cr 2p region of the XPS spectrum of CrN11100.

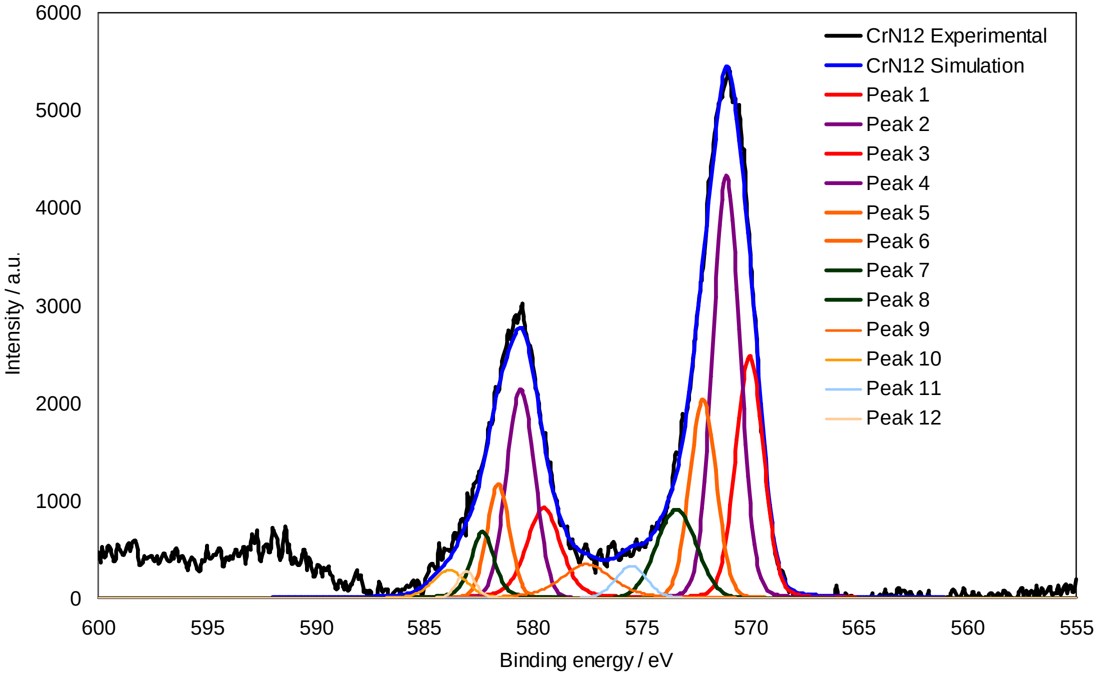

Figure S9c. Cr 2p region of the XPS spectrum of CrN12100.

Hydrogen storage materials	BET sufarce area (m^2/g)	Gravimetric Adsorption (wt%) at 77K, 80 bar	Gravimetric Adsorption (wt%) at 298K, 80 bar	Retention capacity (%)	Adsorption Enthalpy (kJ/mol)
CrN11100	12.08	1.75	0.73	41.71	47.6
CrN11150	9.40	1.47	0.44	30.61	43.4
CrN12100	14.88	1.23	0.34	27.64	42.8
CrN12150	13.10	1.06	0.27	25.47	46.9
CrN21100	32.07	1.56	0.45	28.85	40.4
CrN21150	19.06	1.41	0.36	25.53	39.8
MOF-5	3534	5.10*	0.28*	5.5	3.8*
AX21	3225	4.18	0.55	13.25	5.5

Table S10. Retention capacity, BET surface area and adsorption enthalpy of cyclopentadienyl chromium hydrazide materials compared to MOF-5 and carbon AX-21. (*) From reference 1. All other measurements were conducted in our lab.

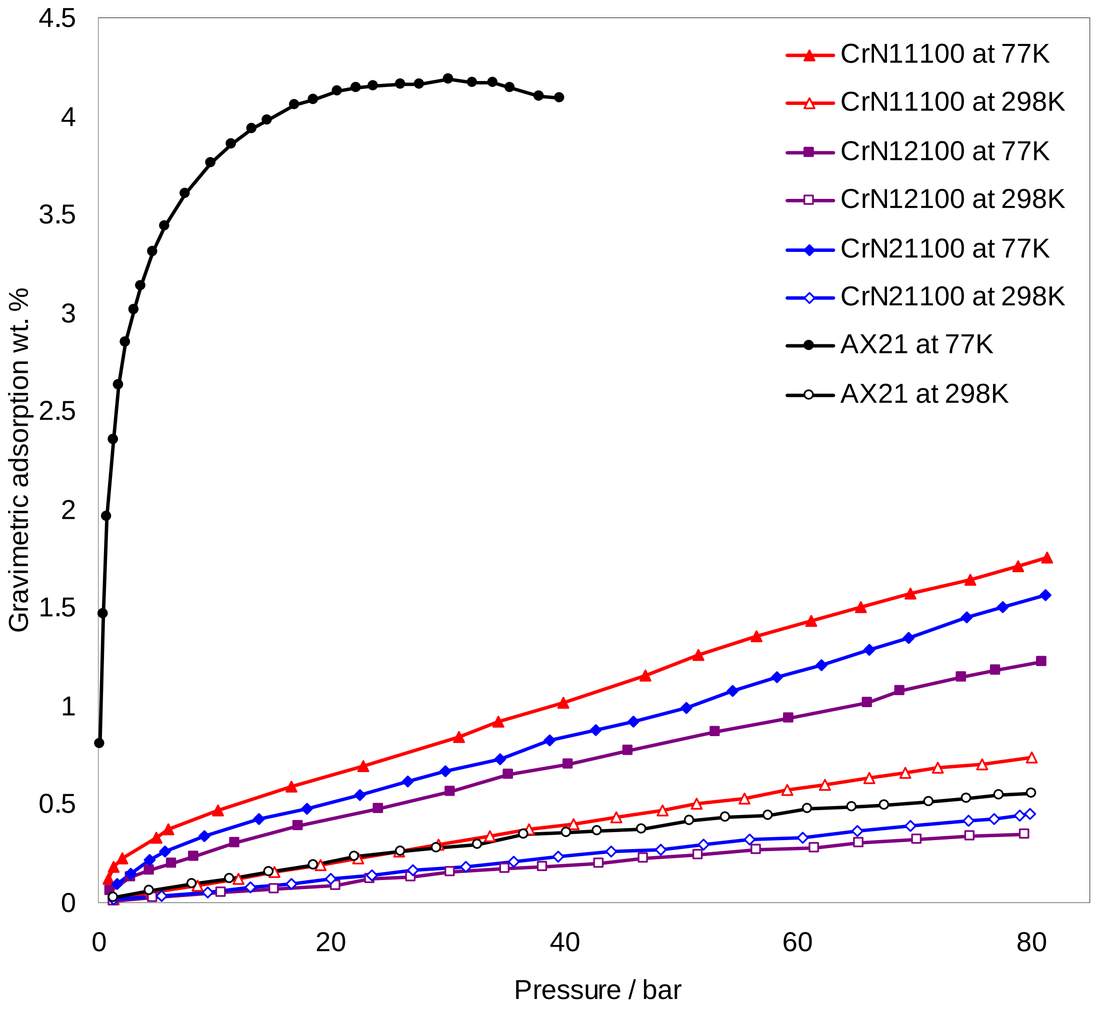

Figure S11. Excess storage isotherms of CrN11100, CrN12100, CrN21100 and carbon AX21 at 77 K and 298 K. (Instrument error range: ± 0.05 wt. %)

	CrN1260	CrN12100	CrN12150	CrN1160	CrN11100	CrN11150	CrN2160	CrN21100	CrN21150
nH_2/Cr (298 K)	0.18	0.27	0.22	0.13	0.40	0.24	0.06	0.20	0.14
nH_2/Cr (77 K)	0.73	0.95	0.85	0.50	0.97	0.80	0.50	0.73	0.54

Table S12. H_2 adsorbed per Cr atom for cyclopentadienyl chromium hydrazide materials.

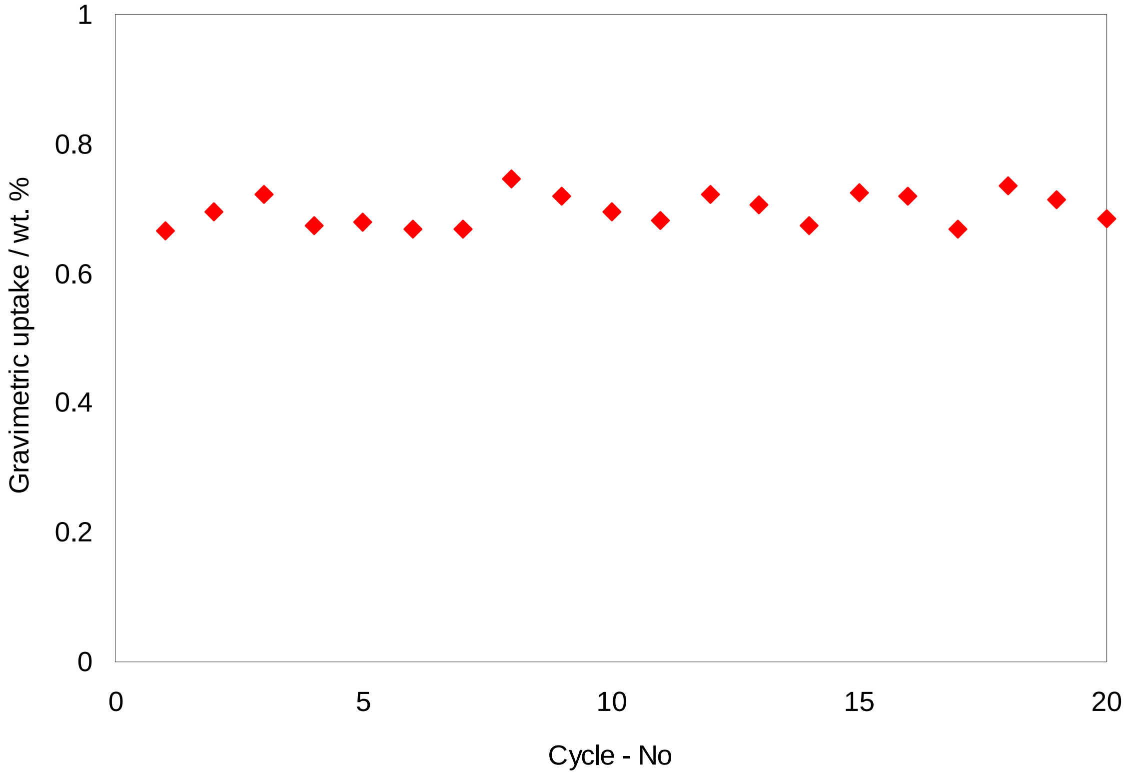

Figure S13. 20 cycles of adsorption and desorption of CrN11100 at 298K and 80 bar.

(Instrument error range: ± 0.05 wt. %)

Reference

1) B. Panella, M. Hirscher, H. Putter, U. Muller, *Adv. Funct. Mater.* **2006**, 16, 520 – 524.