Supporting Information

Hierarchically Porous Reduced Graphene Oxide Coated with Metal–Organic Framework HKUST-1 for Enhanced Hydrogen Gas Affinity

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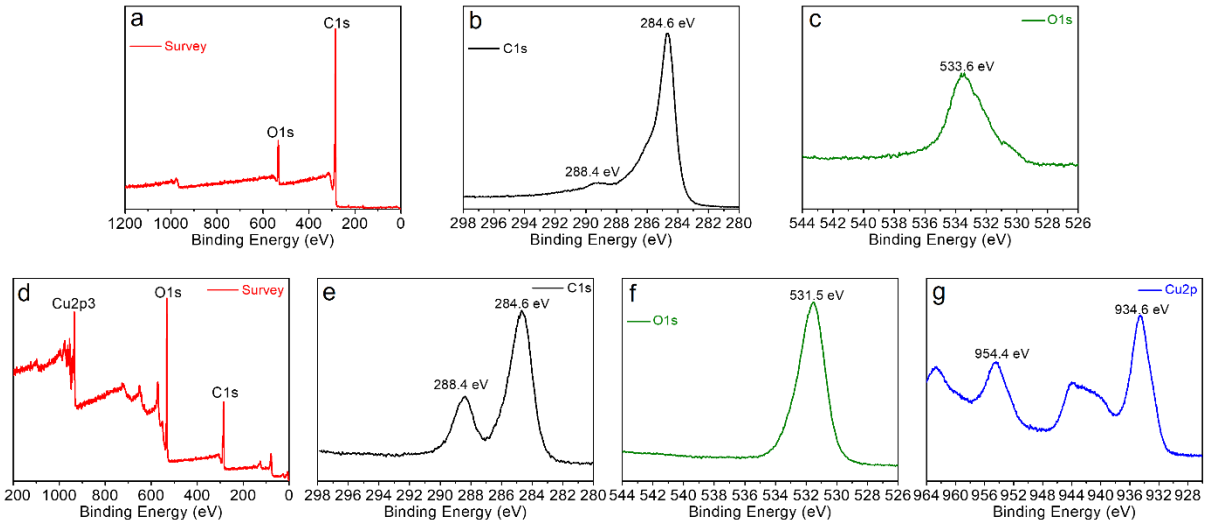

Figure S1. XPS analysis. (a) Survey spectrum, (b) C1s and (c) O1s of HRGO. (d) Survey spectrum, (e) C1s, (f) O1s and (g) Cu2p of HKUST-1.

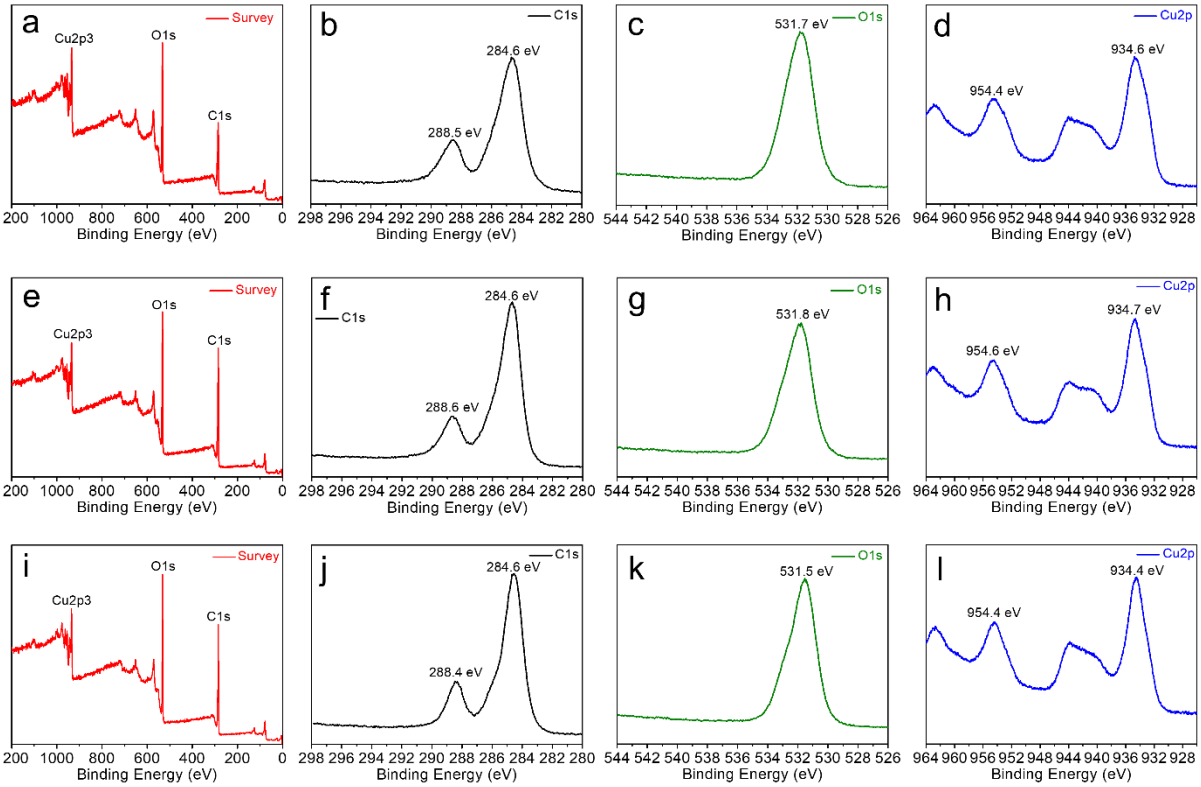

Figure S2. XPS analysis. (a) Survey spectrum, (b) C1s and (c) O1s and (d) Cu2p of HKUST-1@HRGO-10. (e) Survey spectrum, (f) C1s and (g) O1s and (h) Cu2p of HKUST-1@HRGO-15. (i) Survey spectrum, (j) C1s and (k) O1s and (l) Cu2p of HKUST-1@HRGO-20.

Table S1. XPS analysis table for HRGO, HKUST-1, HKUST-1@HRGO series and physically mixed HKUST-1 and HRGO.

Sample (At %)	C1s	O1s	Cu2p3	Total
HRGO	88.54	11.46	-	100
HKUST-1	46.9	45.94	7.16	100
HKUST-1@ HRGO-10	51.31	41.74	6.95	100
HKUST-1@ HRGO-15	63.84	28.17	7.99	100
HKUST-1@ HRGO-20	61	30.66	8.33	100
Physically Mixed HKUST-1 +HRGO	69.35	25.37	5.28	100

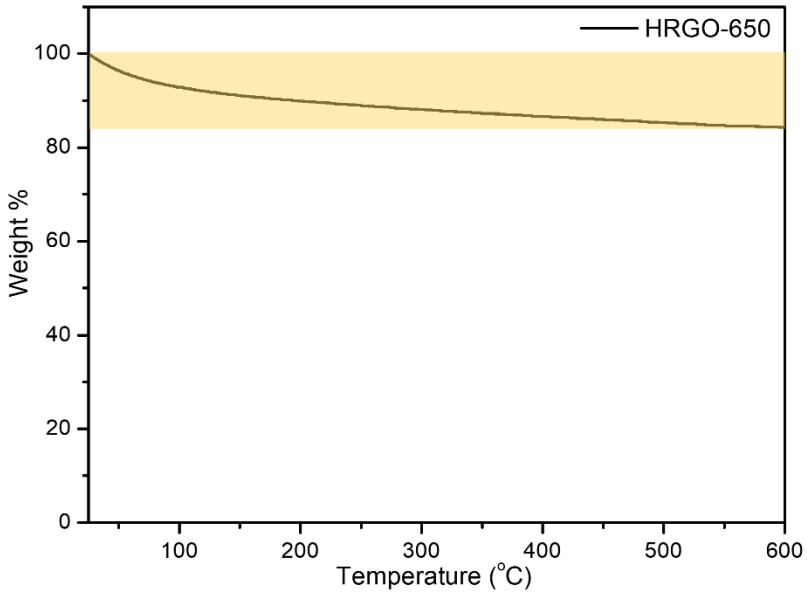

Figure S3. TGA of HRGO under N_2 atmosphere. The weight loss associated with residual oxygen (15.7 wt %) atoms occurred in the temperature range of 25 – 500°C.

Table S2. Inductively coupled plasma-optical emission spectrometry of HKUST-1@HRGO Series

Sample	Copper Concentration (mg/l)	Copper (wt %)
HKUST-1@ HRGO-10	5.77	11.5
HKUST-1@ HRGO-15	4.22	8.5
HKUST-1@ HRGO-20	2.84	5.7

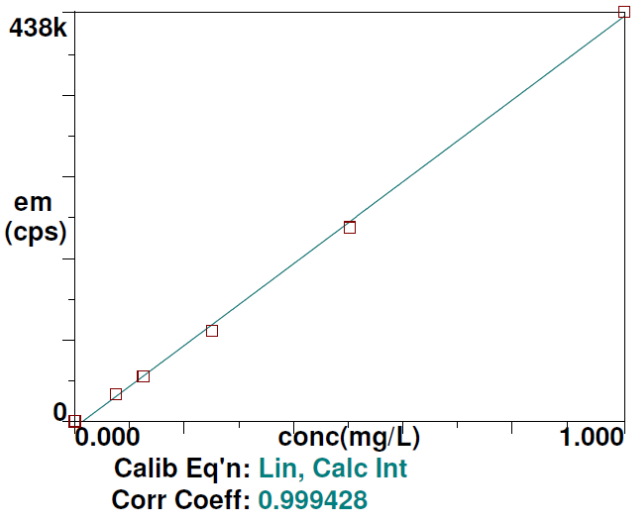

Figure S4. Calibration curve of copper

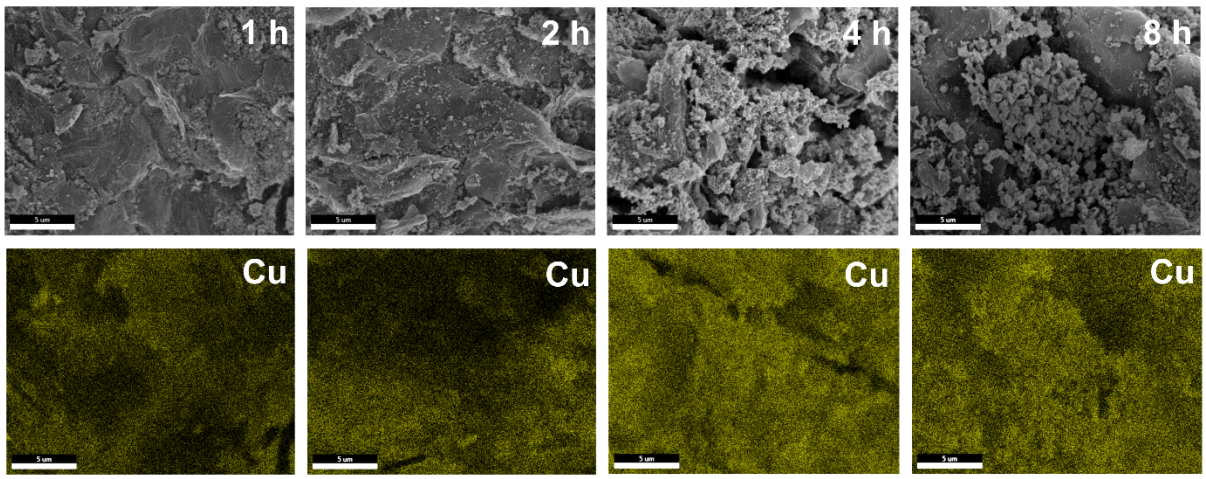

Figure S5. SEM and EDX mapping of time-dependent HKUST-1 growth on HRGO (without washing).

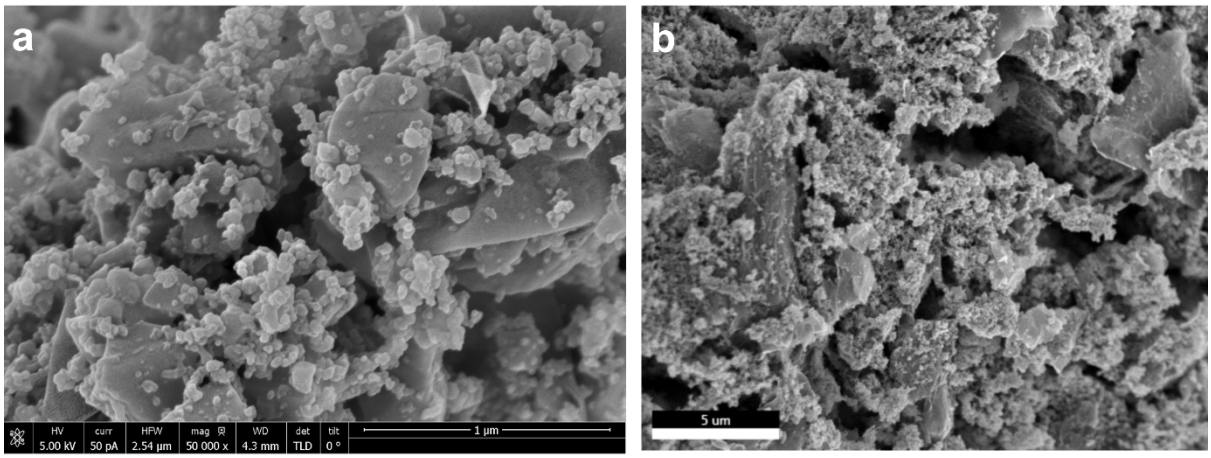

Figure S6. (a) Heterogenous nucleation of HKUST-1 nanoparticles on the surface of HRGO (without w ashing). (b) Filling the macro-/mesopores of HRGO with HKUST-1 nanoparticles (without washing).

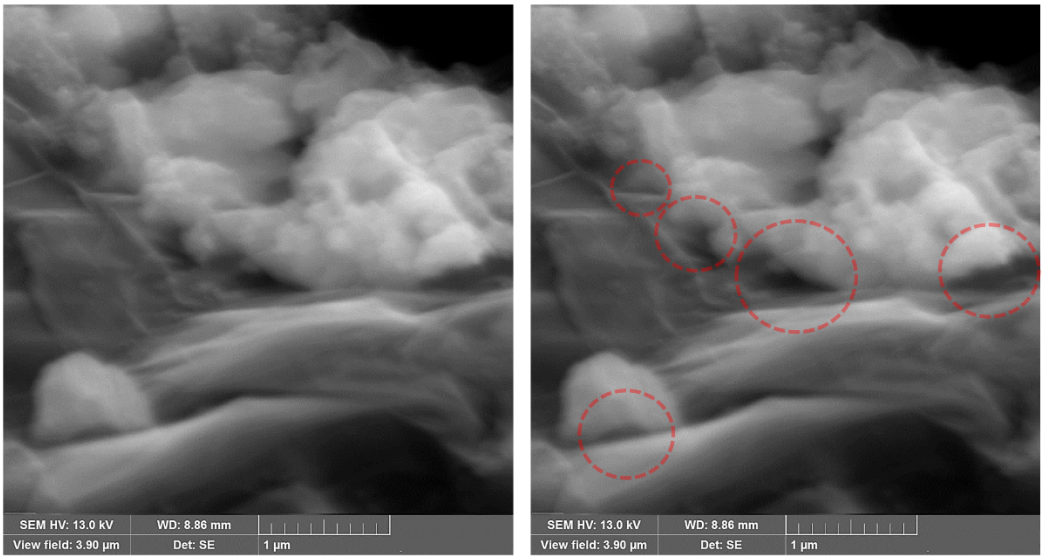

Figure S7. SEM analysis of HKUST-1@HRGO-15 (interfacial pores highlighted by red circles).

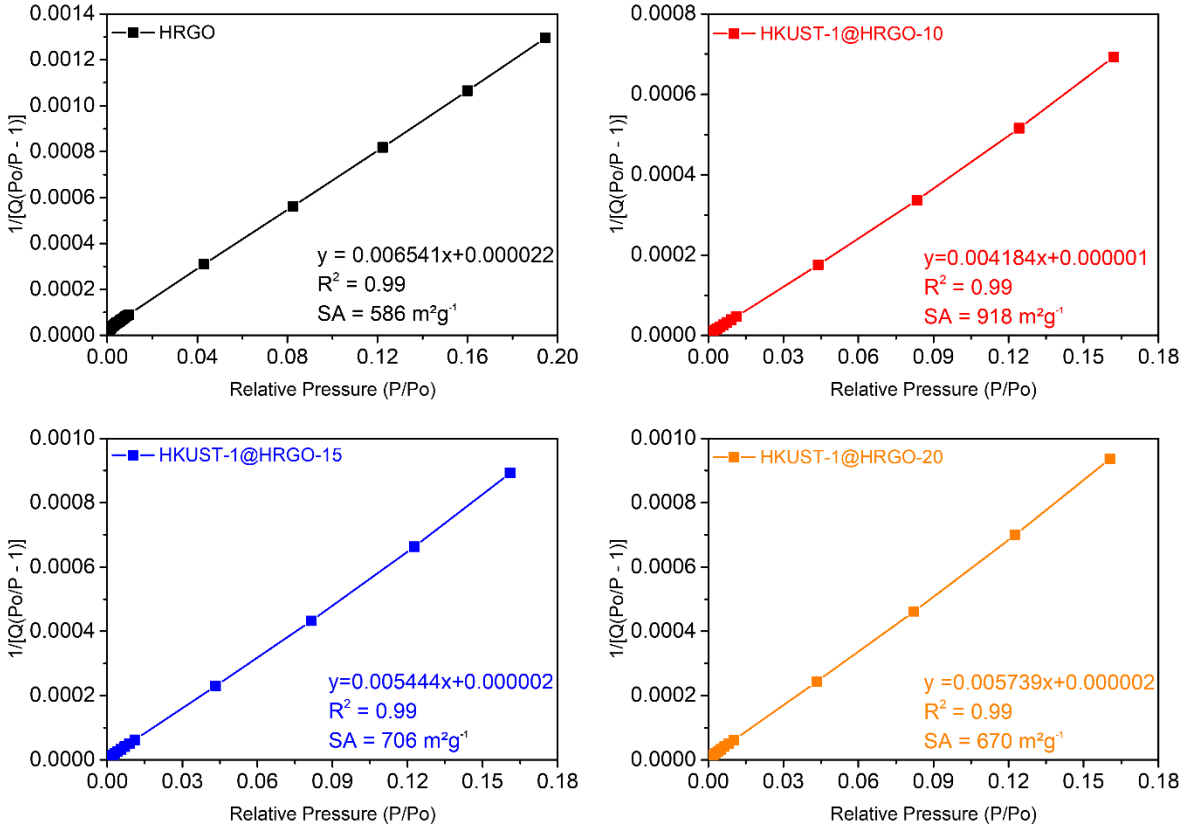

Figure S8. BET linear plots of HRGO, HKUST-1@HRGO-10, HKUST-1@HRGO-15 and HKUST-1@HRGO-20.

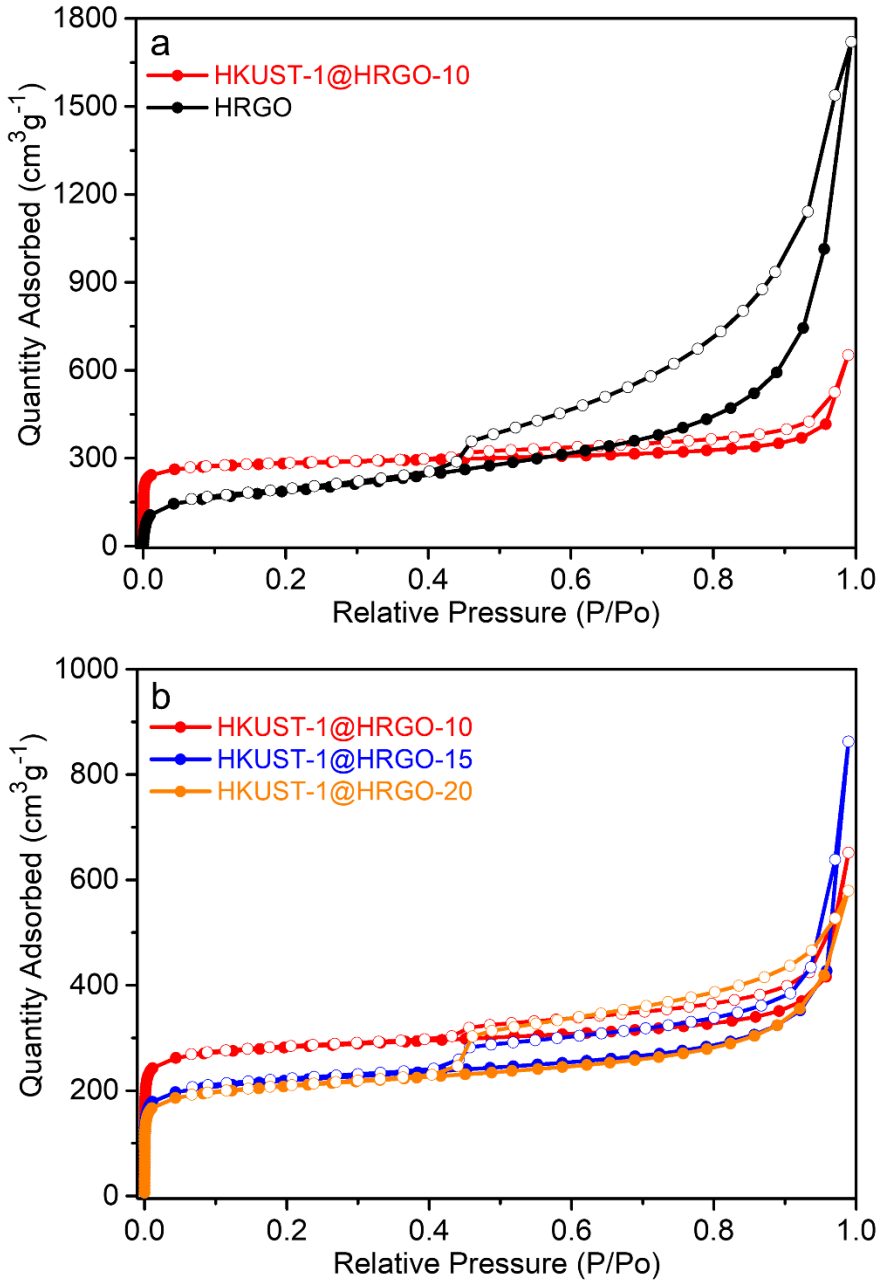

Figure S9. Surface area analysis of HRGO and HKUST-1@HRGO series using Ar at 87 K. (a) The c hange in the Ar adsorption (filled) and desorption (empty) isotherms at 87 K for HRGO and HKUST-1 @HRGO-10. (b) Ar adsorption and desorption isotherms of hierarchically porous HKUST-1@HRGO ser ies at 87 K.

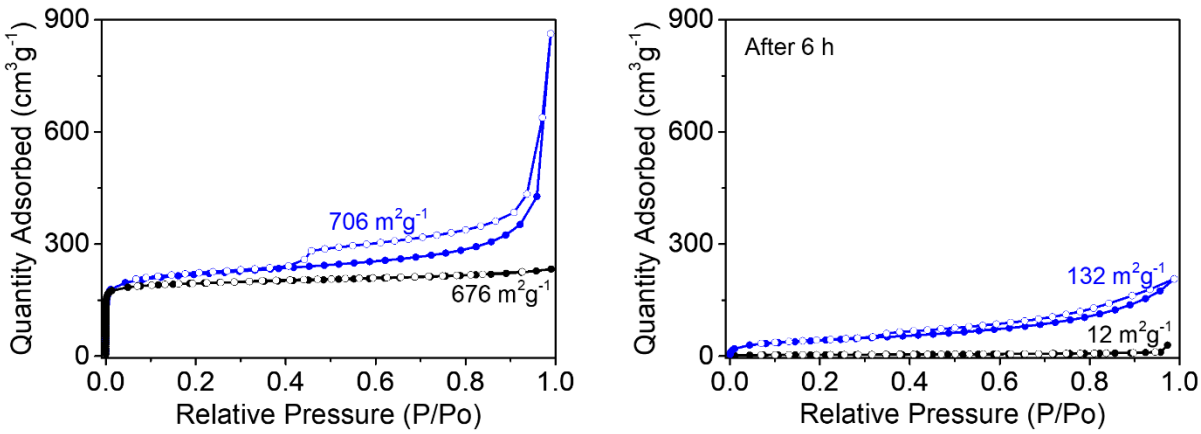

Figure S10. BET surface area analysis of HKUST-1 (black), HKUST-1@HRGO-15 (blue) before and after water treatment.

Table S3. BET surface area analysis of HKUST-1@HRGO-15 before and after H_2 uptake

HKUST-1@HRGO-15	BET [a], (m^2 g^{-1})	S_{micro} [b], (m^2 g^{-1})	S_{ext} [c], (m^2 g^{-1})	V_{total} [d], (cm^3 g^{-1})	V_{micro} [e], (cm^3 g^{-1})	V_{ext} [f], (cm^3 g^{-1})
Before H_2 analysis	706	515	191	1.08	0.25	0.83
After H_2 analysis	728	585	143	1.10	0.22	0.88

[a] Brunauer−Emmett−Teller (BET) surface area calculated over the pressure range (P/P_O) of 0.01−0.11. [b] Micro pore surface area calculated using the t-plot method. [e] $S_{ext} = S_{total} - S_{micro}$. [d] Total pore volume obtained at (P/P_0) = 0.99. [e] Micropore volume calculated using the t-plot method. [f] $V_{ext} = V_{total} - V_{micro}$.