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SHORT ARTICLE

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Nitrogen, Hydrogen, Carbon Dioxide, and Water Vapor Sorption Properties of Three-Dimensional Graphene

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ABSTRACT: The sorption properties of a 3D graphene were measured for a number of gases and water vapor. The N_2 and H_2 isotherms were measured at (77 and 87) K, respectively, while the CO_2 and water vapor isotherms were measured at (273 and 293) K, respectively. The data could be used for characterization and molecular simulation of adsorption/diffusion in carbonaceous adsorbents.

INTRODUCTION

Graphene-based carbon materials have attracted a great deal of research interest because of their intriguing properties such as superior chemical stability, large surface-to-volume ratio, good thermal and electrical conductivities, and mechanical stability,[1−4] etc. Theoretical calculations predict that regular or irregular combinations of sp^3-bonded carbon atoms, curvature, pores, and graphene fragments are advantageous for molecular hydrogen storage.[3−5] Three-dimensional (3D) graphene possesses a relatively large surface area and high aspect ratio, together with a multiple lattice-layered graphitic structure, and thus it is used in many applications.[6,7] Its unique 3D structure is also closer to the pore geometric model described by Steele's 10−4−3 potential,[8] which is popularly used in molecular simulation of adsorption/diffusion in carbonaceous materials. Guan et al.[9] measured the adsorption properties of some gases/vapors on a single wall nanotube, which is a curved graphene plane. However, the sorption properties of hydrogen and other gases or vapors on 3D graphene have not been reported.

In this work, the sorption properties of N_2, H_2, CO_2 and water vapor on 3D graphene are investigated and reported. These isotherms cover a range of experimental pressures and temperatures.

EXPERIMENTAL SECTION

Pure graphite was purchased from Bay Carbon, which was used to synthesize graphite oxides via oxidation by $NaNO_3$, H_2SO_4, and $KMnO_4$ as reported in the literature.[6,7,10,11] The 3D graphene material was prepared by putting the as-prepared graphite oxide into a glass bottle under vacuum that was heated at 150 °C for 45 min.

The adsorption properties of the 3D graphene were measured with a commercial pore and surface analyzer (Quantachrome Adsorb-1). Before the adsorption measurements, ~20 mg of the sample was loaded in the sample cell and degassed at 150 °C overnight and at high vacuum. The morphology of the sample was studied with scanning electron microscopy (SEM, JEOL JSM 6700F).

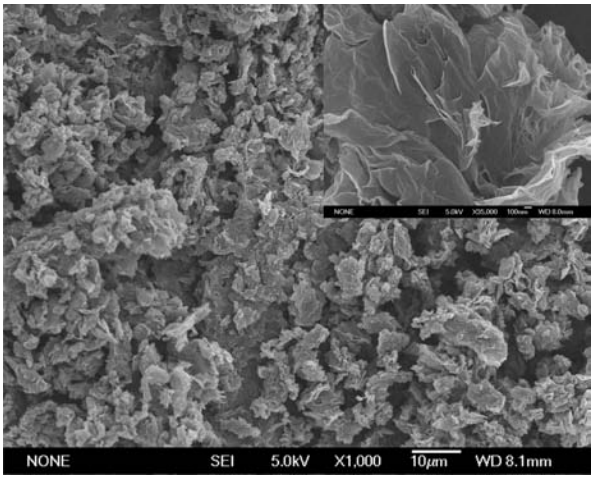

Figure 1. SEM images of 3D graphene.

RESULTS AND DISCUSSION

The SEM image of the sample is shown in Figure 1. It is seen that the material is 3D in structure with sizes ranging from (1 to 10) μm. The magnified morphology of the sample is shown in Figure 1 as the inset, from which we see that the sample consists of multiple layers of graphene flakes with such defects as edges, corners or pores.

Nitrogen adsorption/desorption data were measured at 77 K and are listed in Table 1. Analysis shows that the BET surface area (calculated from the pressure range of $0.06 < P/P_{atm} < 0.3$) is ~477 m^2/g, which is much higher than that of graphite (38 m^2/g) and carbon nanotubes (<200 m^2/g).[12] The total pore volume of the sample is ~1.04 cm^3/g, which may arise from the structural irregularities. DFT analysis shows that the pores are predominantly mesoporous (~4 nm).

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Table 1. Isotherm Data on 3D Graphene

pressure	adsorbed	pressure	adsorbed	pressure	adsorbed
Pa	STPcc·g^{-1}	Pa	STPcc·g^{-1}	Pa	STPcc·g^{-1}
		N_2 (T = 77 K)			
3398.4	65.443	69743	190.97	68068	434.51
6417.9	70.789	72269	198.35	65426	412.52
9081.8	75.227	74742	206.74	62797	392.11
11687	79.111	77202	216.20	60205	372.61
14252	82.791	79417	230.66	57422	356.96
16802	86.402	82003	244.35	55039	338.98
19338	90.091	84377	260.64	52493	321.14
21869	93.889	86699	280.37	50827	291.11
24399	97.775	88693	308.94	47113	166.75
26856	103.10	90767	344.32	44379	157.73
29444	107.37	93485	418.93	41686	151.00
31979	111.58	95721	540.87	39107	144.98
34509	115.82	98271	795.24	36559	139.09
37047	119.92	100256	1300.4	34026	133.16
39584	123.96	99299	1216.7	31483	127.31
41976	130.13	96590	993.15	28870	123.01
44617	134.56	93404	821.65	26392	117.35
47166	138.72	91200	752.90	23856	111.63
49696	142.87	88616	686.62	21314	106.07
52217	147.14	85463	630.01	18769	100.65
54640	154.06	83703	599.83	16228	95.389
57242	158.98	81436	566.48	13698	90.242
59778	163.71	78847	538.42	11191	85.029
62287	168.85	76334	509.05	8666.3	80.248
64789	174.47	73689	481.93	6245.7	75.004
67084	183.66	70843	457.89	4207.0	70.019
		H_2 (T = 77 K)			
58.235	0.32640	8330.0	15.225	104098	146.74
94.819	0.47290	9385.9	17.159	106551	156.91
117.32	0.51140	10463	18.760	99618	145.99
129.06	0.54480	11519	20.245	95032	140.35
136.52	0.55500	12586	22.397	90233	139.49
140.79	0.55560	13652	23.967	85646	133.23
142.92	0.55000	18878	30.899	77007	122.82
143.99	0.53640	24211	38.784	72421	117.64
145.05	0.53030	29544	45.996	67728	113.09
145.05	0.51560	34877	52.366	63141	107.58
222.92	0.70760	40210	58.702	58555	100.64
333.84	0.98130	45436	67.498	53862	96.759
445.83	1.2532	50876	74.001	45116	83.366
554.62	1.5185	56209	80.193	40530	76.035
666.61	1.7552	61542	87.266	35944	70.113
780.74	2.0055	66875	94.130	31357	62.638
891.66	2.2232	72101	102.05	26771	54.852
1002.6	2.4576	77540	108.99	22185	48.309
3989.0	7.9449	82767	118.33	13119	31.977
5119.6	10.187	88206	124.39	8607.3	23.061
6196.8	11.938	93539	130.95	4703.6	17.877
7263.4	13.647	98872	138.53		
		H_2 (T = 87 K)			

Table 1. Continued

pressure	adsorbed	pressure	adsorbed	pressure	adsorbed
Pa	STPcc·g^{-1}	Pa	STPcc·g^{-1}	Pa	STPcc·g^{-1}
61.600	0.17480	7277.1	10.134	98912	120.63
97.100	0.26230	8313.1	12.142	104250	125.78
118.42	0.27030	9399.1	13.736	106594	140.35
130.03	0.27920	10474	15.095	99559	130.01
136.72	0.27250	11540	16.438	95032	124.18
140.36	0.26200	12605	17.781	90503	118.36
142.43	0.24710	13674	19.051	85974	112.63
143.54	0.23340	18905	24.963	77029	103.13
144.30	0.21160	24236	30.902	63232	91.627
144.68	0.18720	29567	36.888	58709	85.514
228.37	0.32870	34836	45.430	54195	79.135
338.39	0.52590	40223	51.787	45144	67.016
449.37	0.71390	45572	57.689	40625	60.762
560.55	0.88200	50909	63.390	31473	51.505
669.49	1.0322	56244	68.936	26956	44.935
780.34	1.2452	61579	74.372	18427	32.272
892.58	1.4076	71961	91.963	13914	25.577
1003.9	1.5490	77545	98.738	9405.3	18.628
4012.4	5.8497	82900	104.51	5201.9	12.969
5135.7	7.4263	88246	109.95		
6207.8	8.8341	93580	115.27		
		CO_2 (T = 273 K)			
78.334	0.033800	40331	5.9148	82308	14.825
116.74	0.019500	45662	6.5811	76971	14.607
346.24	0.11820	50992	7.2814	71641	14.191
573.10	0.20560	56326	7.8664	66311	13.743
796.97	0.27170	61656	8.5481	60982	13.383
1021.6	0.34700	66995	9.1758	55657	12.800
4078.0	1.1515	72326	9.8802	50311	12.449
6228.3	1.5273	77658	10.589	44993	11.747
8354.4	1.9424	82996	11.246	39665	11.115
9421.5	2.2061	88326	11.981	34328	10.449
10496	2.4385	93653	12.659	28997	9.6895
12623	2.7685	98991	13.453	23666	8.9004
13691	3.0346	104312	14.245	18342	8.0028
19016	3.4707	106594	15.156	13014	7.1403
24340	4.0568	98281	15.313	7688.9	6.1130
29672	4.6373	92956	15.205	3515.1	4.7977
34996	5.3273	87616	15.263		
		H_2O (T = 293 K)			
1187.1	1.0262	27405	16.702	97023	232.92
2245.9	1.7948	33476	20.929	96881	251.08
3098.8	2.3781	38717	25.423	95398	224.06
3799.2	2.8099	44969	30.061	94336	197.21
4279.6	3.1540	59246	49.569	94249	170.20
5643.2	4.1270	74631	74.747	89643	146.05
6985.3	4.8903	83007	92.684	89748	120.56
8122.2	5.5619	90419	123.15	86634	107.59
10308	6.6433	93347	148.42	42365	28.128
11605	7.4242	94577	172.80	36968	25.179
16902	9.8675	95291	192.35		
22057	12.973	95882	208.14		

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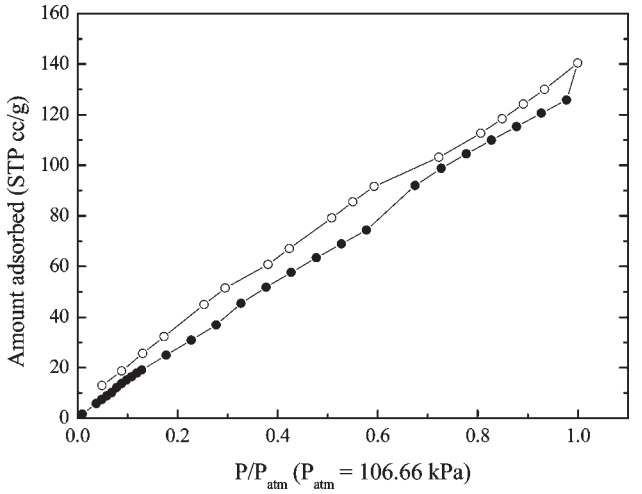

Figure 2. H_2 isotherms on 3D graphene at 87 K. Adsorption data are shown as closed circles; desorption data, as open circles.

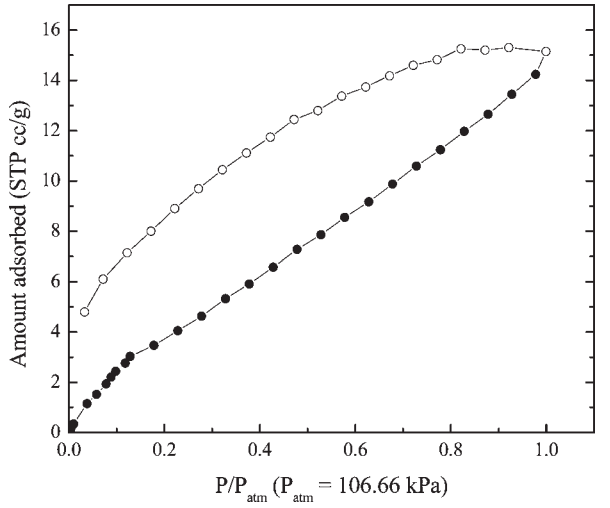

Figure 3. CO_2 isotherms on 3D graphene at 273 K. Adsorption data are shown as closed circles; desorption data, as open circles.

Hydrogen adsorption/desorption data at (77 and 87) K are also listed in Table 1, and the isotherms at 87 K are presented in Figure 2. From Table 1 and Figure 2, it can be determined that the hydrogen storage capacity at 106.6 kPa and (77 and 87) K is (1.40 and 1.25) % (by weight), respectively. The small hysteresis between the desorption and adsorption isotherms may indicate chemisorption also occurs because some residual oxygen functional groups exist in the graphene material.[1,2,6,13] According to our previous work,[6] these functional groups could include epoxy, hydroxyl and carboxyl groups.

Figure 3 shows the adsorption/desorption isotherms of CO_2 on the 3D graphene at 273 K, with the data also listed in Table 1. A clear hysteresis is shown between the desorption and adsorption isotherms. Although this may result from the mesoporosity of the 3D graphene, as the experimental temperature (273 K) is below the critical temperature of carbon dioxide (304 K),[14] such a significant hysteresis at the low adsorption pressure lets us speculate that there are different adsorption mechanisms involved in the CO_2 adsorption on the 3D graphene. For example, the unsaturated sp^2 bonds at the edge of the graphene plane may

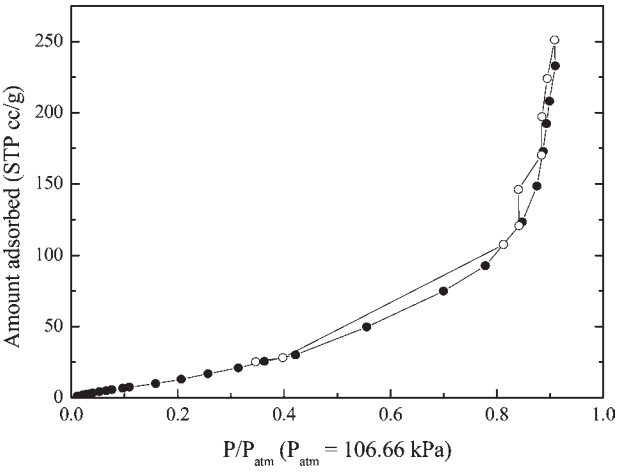

Figure 4. Water vapor isotherms on 3D graphene at 293 K. Adsorption data are shown as closed circles; desorption data, as open circles.

exert strong interaction with the polar CO_2 molecules via strong static electrical interaction. However, the exact mechanism may be left for future research.

The adsorption/desorption isotherms of water vapor were also measured at 293 K as in Figure 4 (the data are listed in Table 1), showing that although capillary condensation does occur in the sample, the observed hysteresis is small, which suggests the 3D graphene material is largely hydrophobic. Since most of functional groups on the graphene surface are hydrophilic, with the capillary condensation effect together they should result in a larger hysteresis, but it is not the case demonstrated by the result. Thus, this result indicates that the amount of the hydrophilic surface functional groups on graphene cannot change its highly hydrophobic nature.

CONCLUSION

The sorption isotherms of N_2 and H_2 were measured for a 3D graphene material at (77 or/and 87) K, while the CO_2 and water vapor isotherms were measured at (273 and 293) K, respectively. The 3D graphene material was found to have a specific surface area of 477 m^2/g, and have mesoporosity centered at 4 nm. The H_2 sorption capacity of the sample was found to be (1.40 and 1.25) % (by weight) at 106.6 kPa and (77 and 87) K, respectively. The CO_2 sorption capacity at 106.6 kPa and 273 K is 2.98% (by weight). The water vapor sorption capacity at 97.0 kPa and 293 K is 18.7% (by weight), and the isotherms indicate that the 3D graphene material is largely hydrophobic.

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