Low temperature reduction of free-standing graphene oxide papers with metal iodides for ultrahigh bulk conductivity

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Supplementary information

1. Conductivity of rGO papers

Table.S1 shows the square resistance (R_{sq}), thickness and conductivity of all rGO papers. The R_{sq} is the average value of 4 measured points on each rGO paper while the thickness is the average value of 5 measured points on each rGO paper. The standard deviation (S.D.) is obtained from 5 samples reduced at each condition.

Table S1 Conductivity of all rGO papers.

Reductants	pH	Sample No.	R_{sq} (Ω/sq)	Thickness (μm)	Conductivity (S/m)	Aver. (S/m)	S. D. (S/m)
FeI_2	0.0	1	9.0	2.2	50269	47738	4379
		2	8.0	2.8	44522		
		3	9.1	2.0	55089		
		4	7.3	3.0	45601		
		5	9.2	2.5	43207		
FeI_2	0.3	1	9.5	2.3	45465	42041	1869
		2	9.8	2.5	40901		
		3	10.3	2.3	42325		
		4	9.6	2.5	41487		
		5	10.4	2.4	40026		
FeI_2	0.5	1	9.9	2.0	50356	44169	4176
		2	10.4	2.4	40190		
		3	10.2	2.2	44443		
		4	9.5	2.7	39059		
		5	10.7	2.0	46794		
FeI_2	0.7	1	10.9	2.6	35334	33907	1459
		2	11.6	2.7	31997		
		3	10.6	2.7	35048		
		4	10.7	2.9	32265		
		5	8.9	3.2	34890		
FeI_2	1.0	1	13.5	2.6	28427	31400	2204
		2	13.6	2.5	29515		
		3	13.5	2.3	32242		
		4	13.5	2.3	32164		
		5	10.7	2.7	34654		
FeI_2	1.5	1	19.7	3.0	16908	15078	3762
		2	28.7	3.8	9160		
		3	21.2	2.5	18908		
		4	24.0	3.4	12231		
		5	15.3	3.6	18182		

FeI_2	2.0	1	33.5	5.4	5524	7161	1842
		2	26.0	3.9	9846		
		3	31.2	5.2	6156		
		4	33.7	5.5	5399		
		5	29.6	3.8	8882		
FeI_2	As ma -de 3.2	1	25.5	4.3	9121	6744	1234
		2	25.1	6.8	5863		
		3	25.3	6.9	5737		
		4	24.6	6.1	6656		
		5	25.4	6.2	6340		
MgI_2	1	1	12.2	2.4	34294	32246	3823
		2	15.3	1.9	34450		
		3	15.1	2.6	25535		
		4	15.3	1.8	36299		
		5	10.9	3.0	30651		
MgI_2	2	1	3167.0	3.3	102	506	610
		2	2866.0	3.5	92		
		3	176.5	3.3	1710		
		4	1051.0	3.6	279		
		5	854.7	3.3	345		
ZnI_2	1	1	17.1	2.5	39089	32074	3780
		2	10.3	4.1	31402		
		3	12.5	3.5	32077		
		4	12.4	3.7	29802		
		5	11.9	4.0	27999		
ZnI_2	2	1	30177.0	2.8	11.0	28.6	48.4
		2	3331.8	2.4	125.0		
		3	645572.5	3.1	0.5		
		4	726750.0	3.6	0.4		
		5	68184.8	2.9	5.0		
AlI_3	1	1	12.5	2.5	31879	33568	2057
		2	12.4	2.5	32135		
		3	12.1	2.2	37519		
		4	11.9	2.5	33543		
		5	10.9	2.8	32765		
AlI_3	2	1	90.3	3.2	3460	2679	536
		2	136.9	3.4	2148		
		3	104.2	3.2	2998		
		4	154.8	3.2	2019		
		5	112.8	3.2	2772		

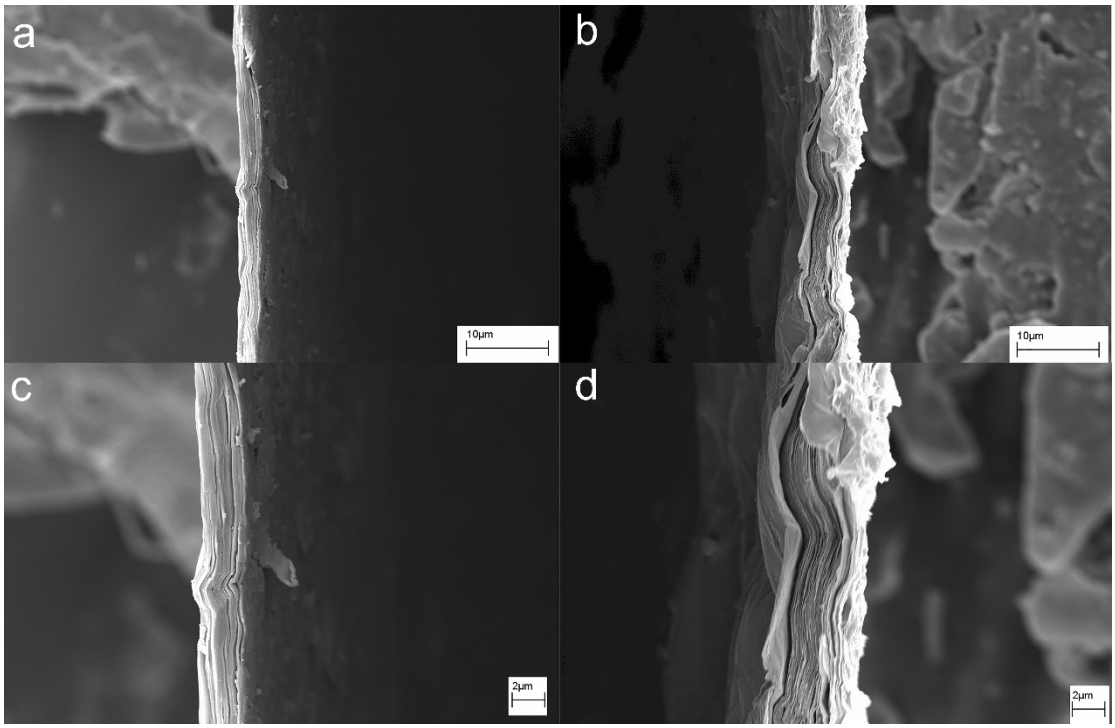

Fig.S1 SEM pictures of GO (a, c) and rGO (b, d) papers.

Fig.S1 shows the cross section of GO and rGO papers. The thickness of GO and rGO papers is around 2 μm.

2. XPS analyze of rGO papers

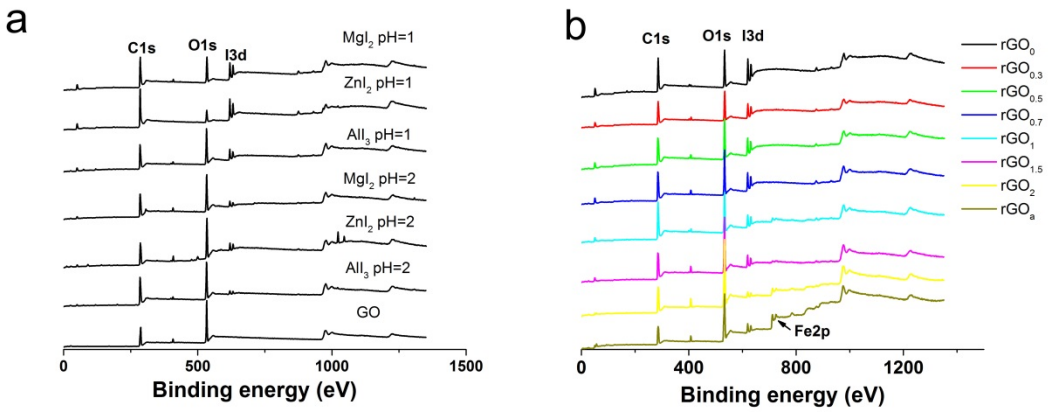

Fig.S2 Full range XPS spectra of GO paper and rGO papers reduced by MgI_2, ZnI_2, AlI_3 (a) and FeI_2 solutions with different pH.

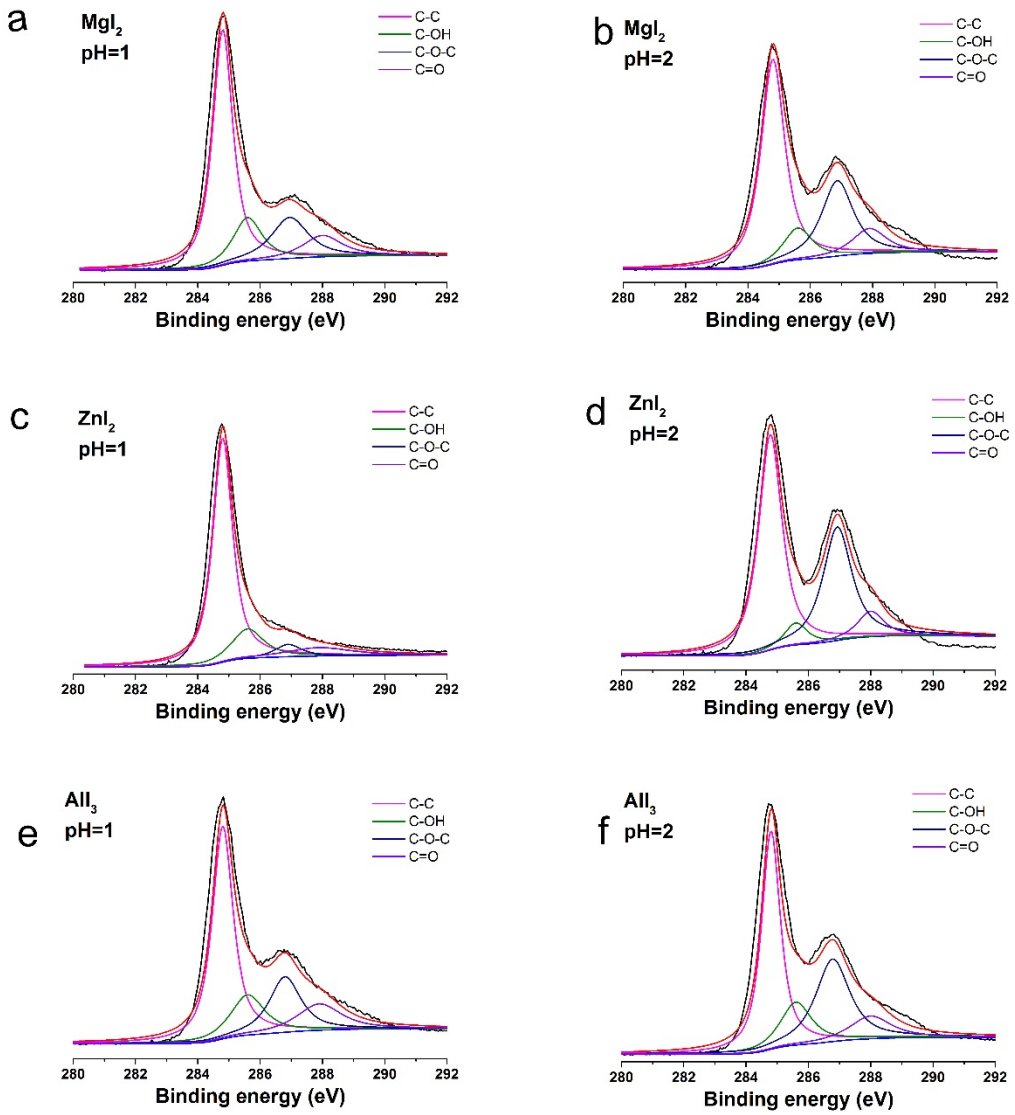

Fig.S3 Deconvolution of C 1s peak of rGO papers reduced by MgI_2, ZnI_2, and AlI_3 solutions with pH=1 and pH=2.

Fig.S2 a shows the full range XPS spectra of rGO papers. Peaks corresponding to C 1s, O 1s and I 3d can be obtained from spectra of rGO papers. rGO papers reduced at low pH (pH ≤ 1) show higher I 3d peak compared with rGO papers reduced at high pH (pH ≥ 2), indicating higher degree of nucleophile substitution reaction. However, the height of C 1s peak and O 1s peak does not show any relationship with the height of I 3d or pH. Moreover, while pH ≥ 1, Fe 2p peak appears (Fig.S2 b), indicating the formation of relatively high amount of hydrolysis products.

Fig. S3 shows that MgI_2, ZnI_2, and AlI_3 solutions with pH=1 has much stronger reductive ability than those solutions with pH=2 and the relative content of C-O-C increases as pH increases.

Table S2 shows the summary of XPS results. It is noteworthy that the C/O ratio may decrease after the reduction while the conductivity greatly increases for rGO papers reduced with pH ≥ 2. However, by deconvolution of C 1s peak, it is clear that

the content of all kinds of carbon-oxygen bonds decreases compared with GO. Then, the decrease of C/O ratio must be caused by the formation of other oxides, which must be the products of hydrolysis reaction.

Table S2 XPS analyze of rGO papers reduced at different conditions.

Reductants	pH	C (at %)	O (at %)	Fe (at %)	C/O
FeI_2	0	71.10	28.76	0.14	2.47
FeI_2	0.3	69.30	30.70	0.00	2.26
FeI_2	0.5	68.63	31.37	0.00	2.19
FeI_2	0.7	67.25	32.57	0.18	2.06
FeI_2	1	61.47	38.11	0.42	1.61
FeI_2	1.5	68.80	28.72	1.56	2.39
FeI_2	2	53.93	44.92	1.15	1.20
FeI_2	3.2 (as made)	49.98	47.02	3.01	1.06
MgI_2	1	75.85	24.15	\	3.14
MgI_2	2	64.72	35.28	\	1.83
ZnI_2	1	88.82	11.18	\	7.94
ZnI_2	2	63.04	36.96	\	1.70
AlI_3	1	64.89	35.11	\	1.85
AlI_3	2	68.04	31.96	\	2.13
GO	\	58.55	41.45	\	1.41

3. Raman analyze of rGO papers

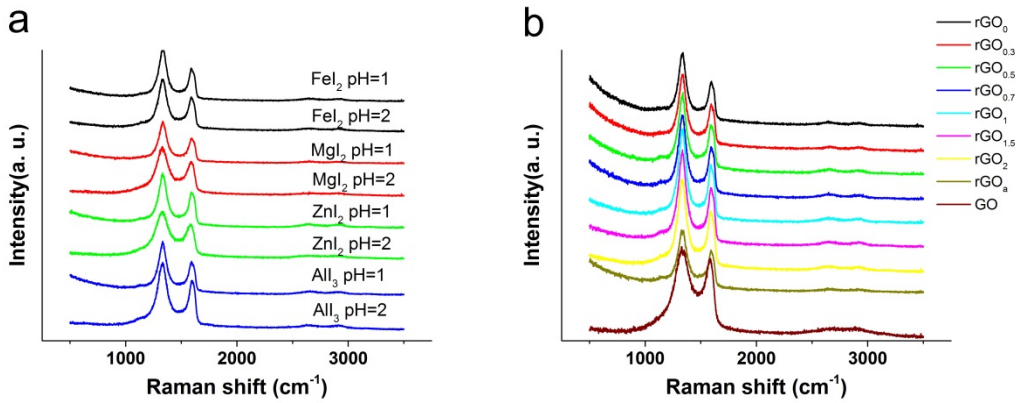

Fig.S4 Raman spectra of rGO papers reduced by FeI_2, MgI_2, ZnI_2, AlI_3 solutions (a) and GO paper and rGO papers reduced by FeI_2 solution with different pH (b).

Raman spectra of all rGO papers show increased I_D/I_G compared with Raman spectrum of GO paper, indicating decreased defect concentration in rGO papers. Moreover, the spectrum of GO paper shows a higher hollow site between two peaks (larger distance in height between the hollow site and flat part at right side) compared with the spectra of rGO papers. Fig.S4a shows that rGO papers reduced by MgI_2, ZnI_2 and AlI_3 with pH=2 have higher hollow site compared with those reduced with pH = 1, indicating rapidly decreased reductive ability of metal iodides

as pH increases. However, the high hollow site is not observed in the rGO papers reduced by FeI_2 with pH=2, indicating reasonable reductive ability of FeI_2 when pH = 2. Fig.S4b shows that the shape of spectra and I_D/I_G of rGO papers reduced by FeI_2 are inert to of pH.

The results of Raman measurement are summarized in table S3. It can obtained from table S3 that I_D/I_G shows a relative high decrease only when pH > 2, which further proves that I_D/I_G is inert to the change of pH.

Table S3 Raman analyze of rGO papers reduced at different conditions.

Reductants	pH	I_D (a. u.)	I_G (a. u.)	I_D/I_G
FeI_2	0	375.9	229.8	1.55
FeI_2	0.3	402.4	251.9	1.60
FeI_2	0.5	389.3	250.4	1.66
FeI_2	0.7	377.2	237.5	1.59
FeI_2	1	394.1	234.5	1.68
FeI_2	1.5	410.1	257.2	1.59
FeI_2	2	564.9	389.6	1.45
FeI_2	3.2	311.4	211.0	1.48
MgI_2	1	348.2	215.2	1.62
MgI_2	2	403.8	288.3	1.40
ZnI_2	1	455.9	307	1.48
ZnI_2	2	394.6	294.7	1.34
AlI_3	1	446.5	286	1.56
AlI_3	2	589.6	425.5	1.38
GO	\	499.7	462.5	1.08