Electronic Supplementary Information (ESI)

Effective low temperature reduction of graphene oxide with vanadium (III)

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1. Graphene oxide

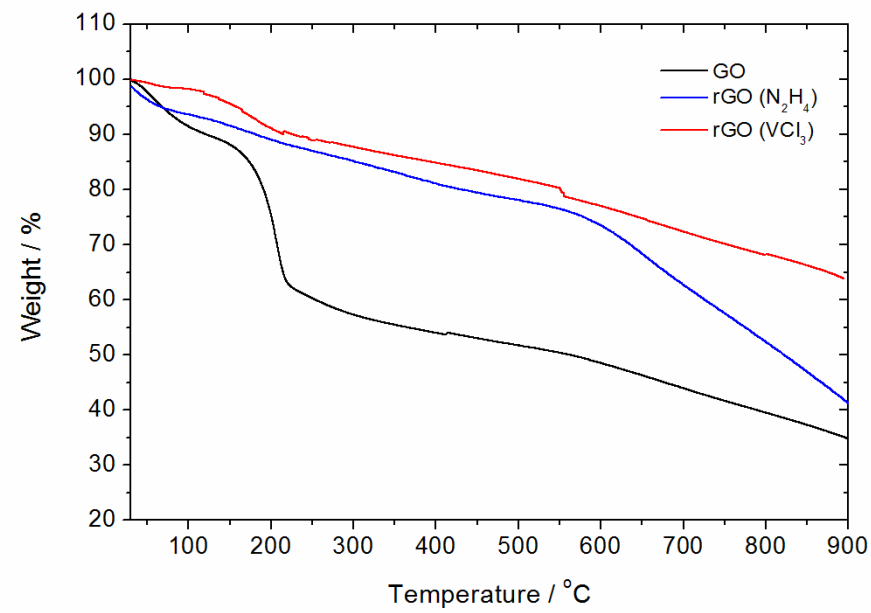

Fig. S1 Thermal gravimetric analysis for GO, rGO (N_2H_4) and rGO (VCl_3) from 30 °C to 900 °C with 5 °C/min heating rate in nitrogen.

Graphene oxide showed circa 30 %, mass loss around 200 °C. This mass loss is related to removal of oxygen functional groups which are mainly located in the oxidation debris attached to graphene oxide sheets. Samples reduced with hydrazine and VCl_3 showed only 5 and 7 % losses, respectively. rGO(VCl_3) was prepared by reacting 20 mM VCl_3 with GO (1.0 mg/ml) for 45 min at 95 °C. rGO (N_2H_4) was prepared similarly using 0.25 mg/ml GO solution and 5.7 mM hydrazine.

2. Reduction of GO with VCl_3

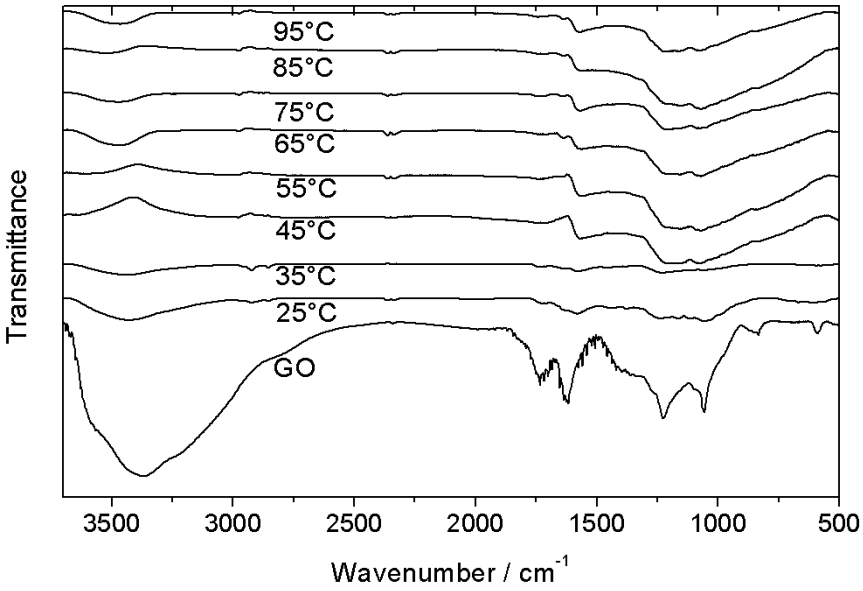

Fig. S2 FT-IR spectra of GO (1.0 mg/ml) reduced with 20 mM VCl_3 for 45 min at different temperatures.

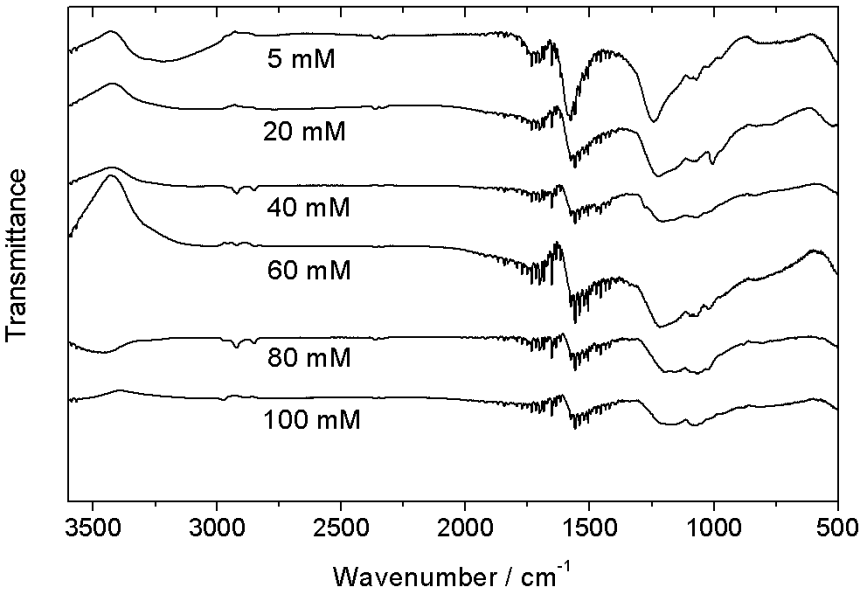

Fig. S3 FT-IR spectra of GO (1.0 mg/ml) reduced with different VCl_3 concentrations for 45 min at 95 °C.

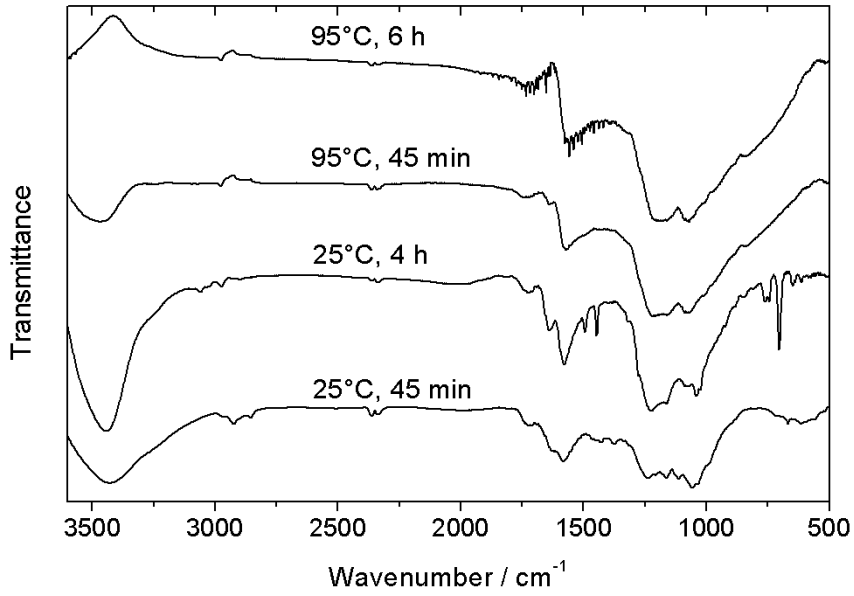

Fig. S4 GO reduced in 20 mM VCl_3 solution at 95 °C for 45 min and 6 hours and at 25 °C for 45 min and 4 hours.

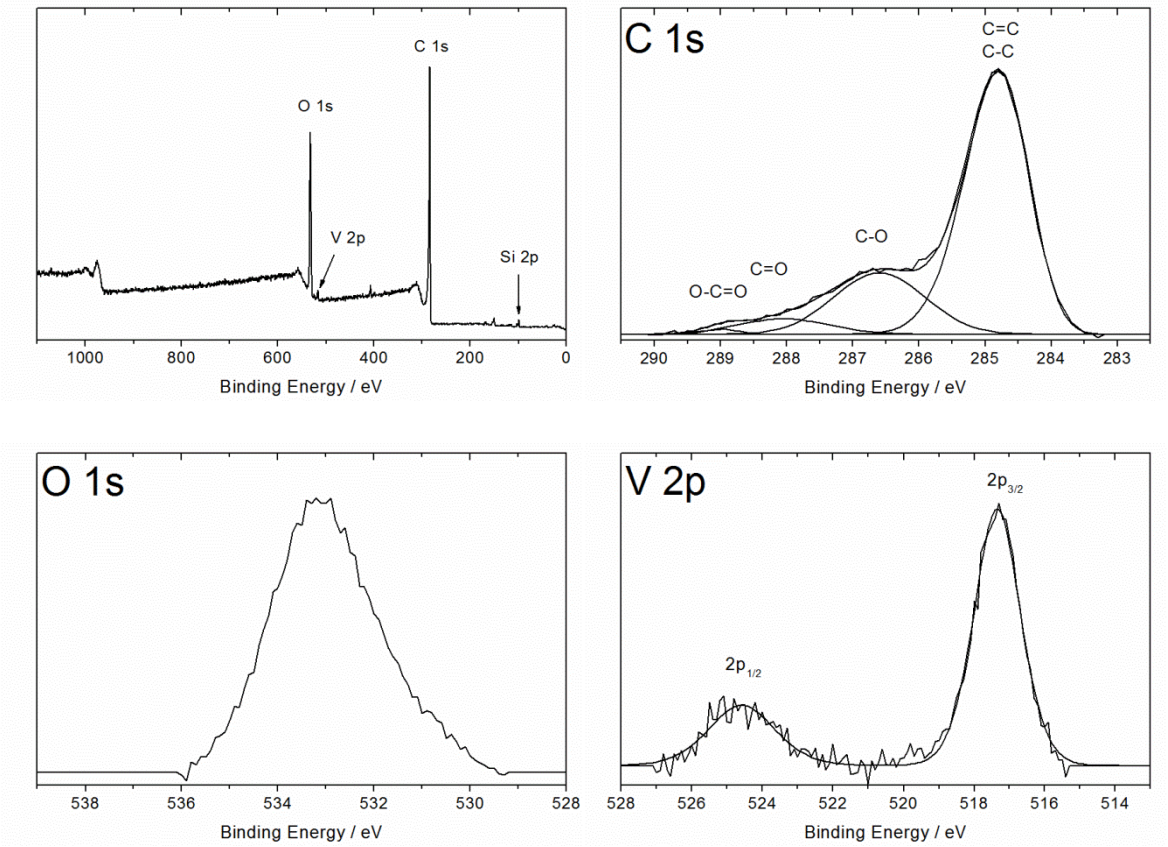

Fig. S5 XPS survey spectrum and C, O and V spectra of rGO sample reduced with VCl_3 at 95 °C for 45 min.

Table S1. Relative fractions of carbon-carbon, carbon-nitrogen and carbon-oxygen bonds in GO and rGO samples.

Sample	C=C/C-C (284.8 eV)	C-N (286.0 eV)	C-O/C=O total	C-O (286.9 eV)	C=O (288.0 eV)	O-C=O (289.0 eV)
GO	44.5 %		55.5 %	45.4 %	7.7 %	2.4 %
rGO(VCl_3, 25 °C)	50.5 %		49.5 %	40.3 %	5.4 %	3.8 %
rGO(VCl_3, 35 °C)	65.8 %		34.2 %	26.3 %	6.2 %	1.7 %
rGO(VCl_3, 45 °C)	65.3 %		34.7 %	29.9 %	2.8 %	2.0 %
rGO(VCl_3, 55 °C)	65.5 %		34.5 %	29.6 %	3.2 %	1.7 %
rGO(VCl_3, 65 °C)	67.6 %		32.4 %	27.3 %	3.9 %	1.2 %
rGO(VCl_3, 75 °C)	69.6 %		30.4 %	23.2 %	5.8 %	1.4 %
rGO(VCl_3, 85 °C)	70.3 %		29.7 %	23.4 %	5.3 %	1.0 %
rGO(VCl_3, 95 °C)	70.3 %		29.7 %	23.1 %	5.9 %	0.7 %
rGO($TiCl_3$, 95 °C)	70.7 %		29.3 %	22.4 %	6.1 %	0.8 %
rGO(N_2H_4, 95 °C)	73.5 %	12.5 %	14.0 %	7.4 %	4.0 %	2.6 %

Table S2. Atomic C/O ratios of GO and rGO samples calculated from XPS results.

Sample	C/O ratio
GO	2.3
rGO(VCl_3, 25°C)	2.5
rGO(VCl_3, 35°C)	3.7
rGO(VCl_3, 45°C)	3.3
rGO(VCl_3, 55°C)	3.4
rGO(VCl_3, 65°C)	3.7
rGO(VCl_3, 75°C)	3.3
rGO(VCl_3, 85°C)	3.5
rGO(VCl_3, 95°C)	4.0
rGO($TiCl_3$, 95°C)	[a]
rGO(N_2H_4, 95°C)	4.0

[a] Due to excess TiO_2 in the sample the contributions of rGO and TiO_2 to the total oxygen content could not be reliably estimated.

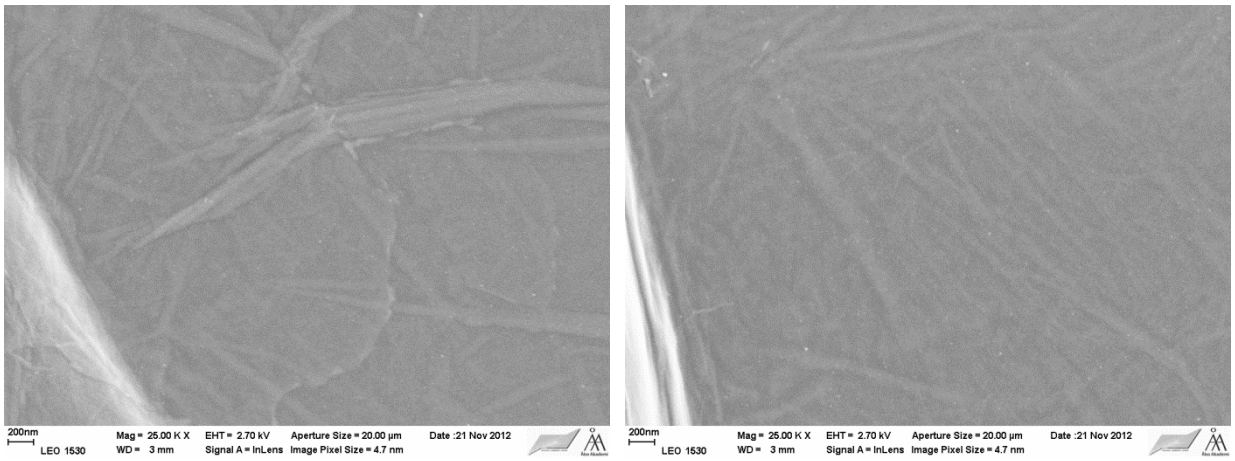

Fig. S6 SEM images (25000 magnification) of GO films before (left) and after (right) reduction with VCl_3.

3. Other reducing agents

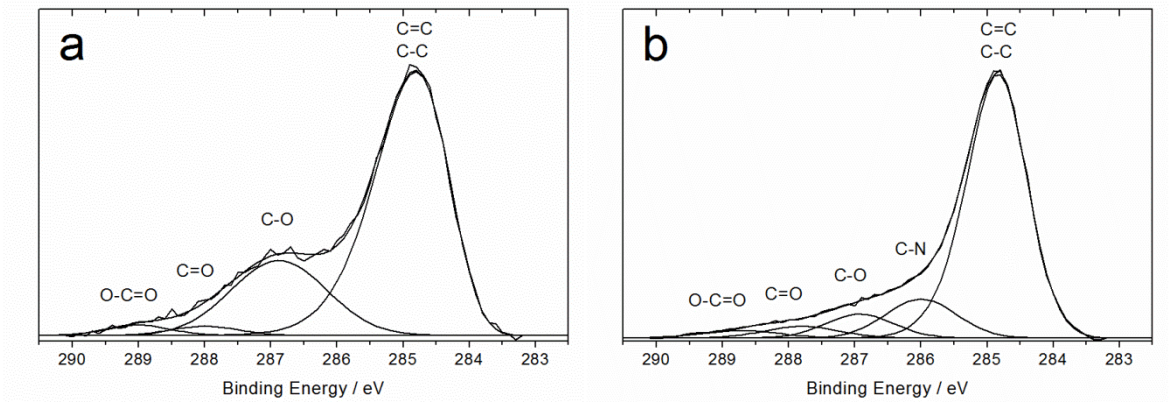

Fig. S7 C 1s XPS spectra of $TiCl_3$ (a) and hydrazine (b) reduced GOs.

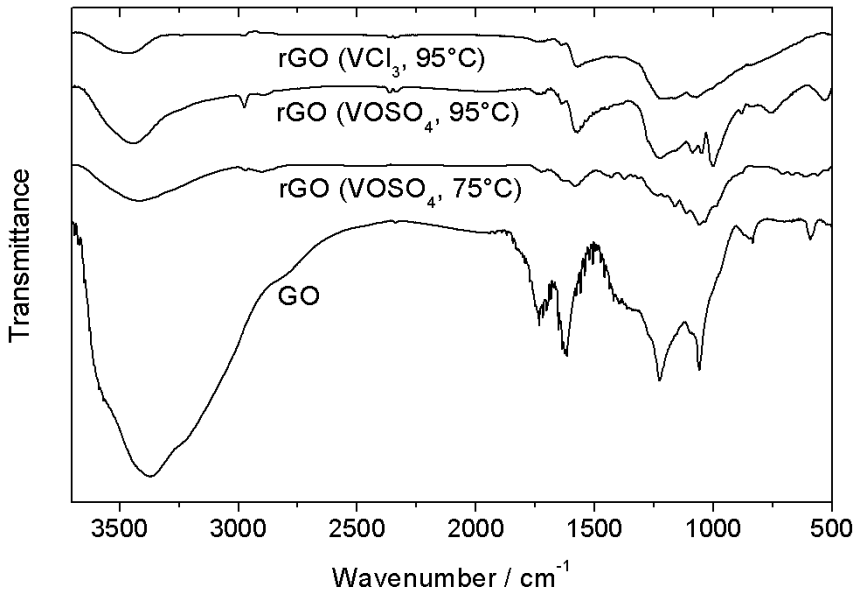

Fig. S8 FT-IR spectra of GO (1.0 mg/ml) and GO reduced with 20 mM V(IV)OSO_4 and 20 mM V(III)Cl_3 for 45 min.

Sheet resistance of GO film reduced with 20 mM $VOSO_4$ at 75°C for 45 min was measured with 4-probe technique. The sheet resistance was $3.2 \cdot 10^3$ Ω/sq which is in the same range to the values of the films reduced with VCl_3.

4. Vanadium +3, +4, +5 and reaction mixture

10 mM solutions of VCl_3, $VOSO_4$ and V_2O_5 were prepared in aqueous HCl solution (pH 1.83, which is same as that of the sample solutions). V_2O_5 was only partially dissolved and, therefore, the solution was filtered before the UV-Vis measurement.

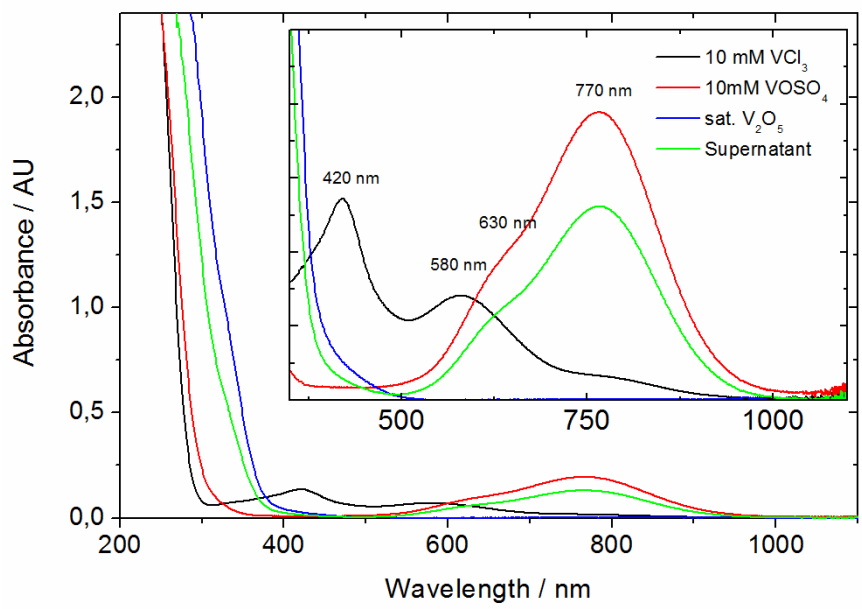

Fig. S9 UV-Vis spectra of solution of vanadium with oxidation states 3+, 4+ and 5+ made from VCl_3, $VOSO_4$ and V_2O_5, respectively. After reduction of GO with 10 mM VCl_3, the supernatant solution was collected and its spectrum measured. Supernatant solution shows signs of V(IV) and V(V) but no V(III) can be seen.

In order to monitor the changes in the redox state of the vanadium species during the GO reduction, graphene oxide was reduced with VCl_3 using an excess of GO. The GO solution (3 mg/ml) was bubbled with argon in a 3-neck bottle and heated to 95 °C under argon flow. VCl_3 (final concentration of 10 mM) was added to GO solution. Samples were taken from the reaction mixture and, after removal of rGO (5 min centrifugation at 50000 G and filtering through 0.45 μm filter), their UV-Vis spectra were measured. After 45 minutes, pH of the supernatant solution of the

reaction mixture was 1.83. The absorption band formed around 800 nm is characteristic of the V(IV) redox state. In addition, the slow decrease of this absorption and the concomitant red shift of the high-rising absorption band below 400 nm signifies the slow disproportionation of V(IV) to V(V) (strong absorption below 400 nm) and V(III) (weak absorption above 400 nm only).

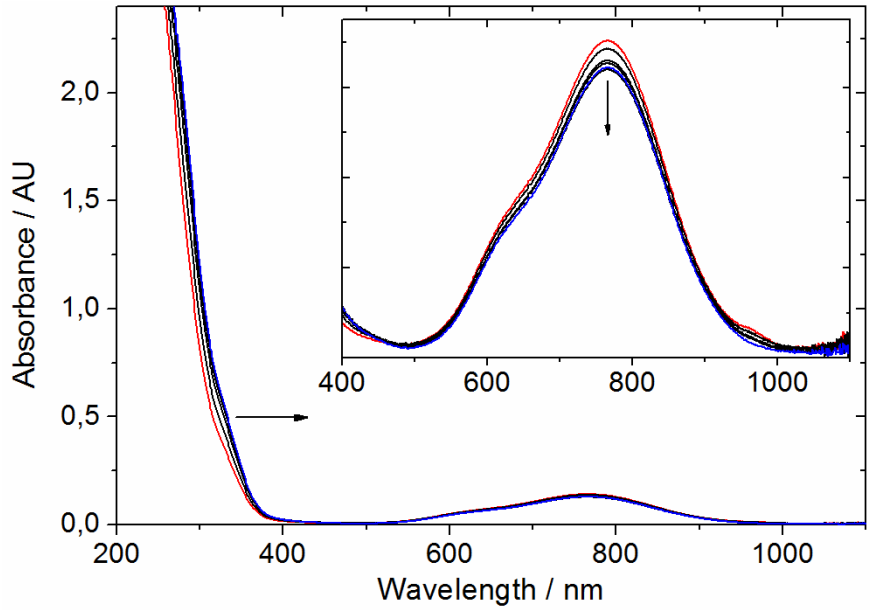

Fig. S10 UV-Vis spectra of samples taken during reduction of GO with VCl_3. Samples were taken at 11 (red), 16, 24, 31, 38 and 45 min (blue).

5. Reduction in organic solvents

When reduced in organic solvents, freeze dried graphene oxide was used in stead of aqueous graphene oxide solution. Acetonitrile and ethanol were used as received. Figure S10 shows the infrared spectra of the reduced GO's.

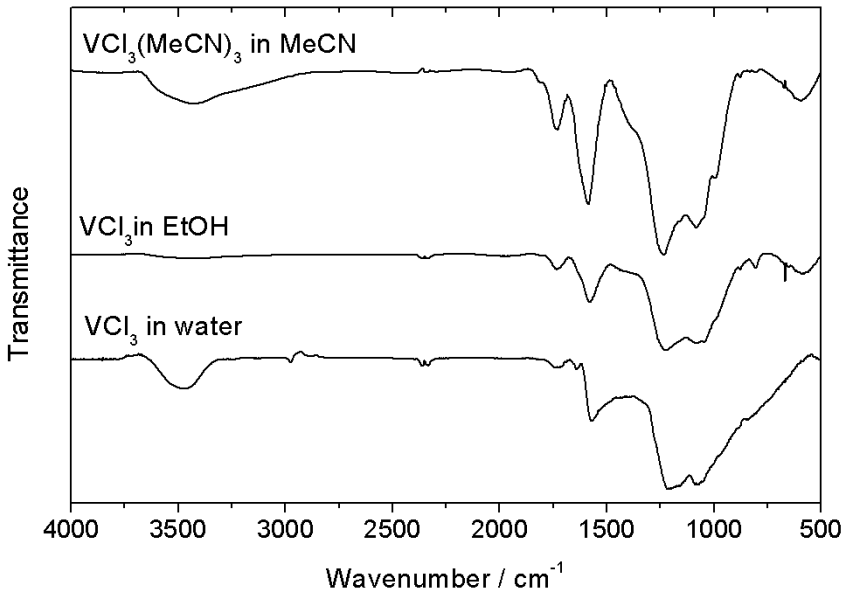

Fig. S11 FT-IR spectra of GO reduced with 20 mM VCl_3 in H_2O, EtOH, and with 20 mM $VCl_3(MeCN)_3$ in MeCN at 75 °C for 45 min.

Table S3 Sheet resistances of VCl_3 reduced GO films at various reduction conditions.

Solvent	c(VCl_3)	Time	Temperature	Sheet Resistance
MeCN	20 mM	45 min	75 °C	$6.6 \cdot 10^4$ Ω/sq
EtOH	20 mM	45 min	75 °C	$7.8 \cdot 10^3$ Ω/sq
H_2O	20 mM	45 min	75 °C	$3.3 \cdot 10^3$ Ω/sq
H_2O	20 mM	240 min	25 °C	$2.4 \cdot 10^3$ Ω/sq