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Supporting Information

One-step molybdate ion assisted electrochemical synthesis of α-MoO_3-decorated graphene sheets and its potential applications

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In this study, we performed the electrochemical exfoliation of graphite in sodium molybdate aqueous solution to obtain scale and large-area graphene sheets. Many different concentration of electrolyte for the electrochemical exfoliation, including 0.05, 0.15, 0.2 and 0.3 M, have been examined. In addition, when 0.2 M Na_2MoO_4 solution was used as an electrolyte, the static potential of 5, 10 and 15 V were investigated. Based on above experimental results, it can be concluded that the static potential of 10 V exhibit ideal exfoliation efficiency when the 0.2 M Na_2MoO_4 solution was used as an electrolyte.

Meanwhile, we found that the exfoliation using only Na_2MoO_4 shall produce the graphene sheets with large amounts of defects as demonstrated in electrical conductivity results. The graphene sheets were possibly oxidized by O_2 produced on the anode. Therefore, the reducing agent $Na_2S_2O_4$ was added to the electrolyte solution.

From the case of exfoliation shown in **Table S1**, the following results were obtained.

(1) Work Voltage Dependence: If the working voltage is small (< 10V), the exfoliation process become very slow and inefficient. When the voltage is increased to the value larger than 10 V, the exfoliation rate is too fast and large graphite particles and thick graphene layer are easily observed. Therefore working bias voltage is optimised at around 10 V.

(2) Concentration Dependence: If the concentration of the Na_2MoO_4 electrolyte is changed from 0.05 to 0.3 M while the working voltage is fixed at 10 V, only the 0.2 M Na_2MoO_4 electrolyte exhibit ideal exfoliation efficiency. When the concentration is small (< 0.2 M), the exfoliation rate is very slow. The concentration is larger than 0.2 M, the electrolyte decomposed and exfoliation rate are fast, large graphite particles are easily observed.

Table S1. Summary for the electrolytes tested in our exfoliation experiments.

Electrolyte	Voltage	Results
Na_2MoO_4 (0.05 M, 40 mL)	10 V	We can get exfoliated sheets but low yield.
Na_2MoO_4 (0.15 M, 40 mL)		We can get exfoliated sheets but low yield.
Na_2MoO_4 (0.2 M, 40 mL)		We can get large amounts of exfoliated sheets.
Na_2MoO_4 (0.3 M, 40 mL)		We can get exfoliated sheets but the exfoliation rate is fast.
Na_2MoO_4 (0.2 M, 40 mL)	5 V	We can get exfoliated sheets but low yield.
	15 V	We can get exfoliated sheets but low yield. And the exfoliation rate is fast.
Na_2MoO_4 (0.2 M, 40 mL) + $Na_2S_2O_4$(1.5 g)	5 V	We can get exfoliated sheets but low yield.
	10 V	We can get large amounts of exfoliated sheets.
	15 V	We can get exfoliated sheets but low yield. And the exfoliation rate is too fast.

Measurement of electrical conductivity

The samples were pressed into a disc of 1.5 cm diameter and typically 2 mm thickness by pressing under 50 MPa at the room temperature. The electrical conductivity was recorded by SDY-V four-point probe instrument (Huayan Instrument Co., China). At least six separate locations were analyzed for each sample and the average was adopted.

The preparation of film

The α-MoO_3-decorated graphene sheets were dispersed in DI water solution by gentle water-bath sonication for 30 min. To remove unwanted large graphite particles produced in the exfoliation, the suspension was subjected to centrifugation at 1500 rpm. The centrifuged suspension can be used for film preparation.

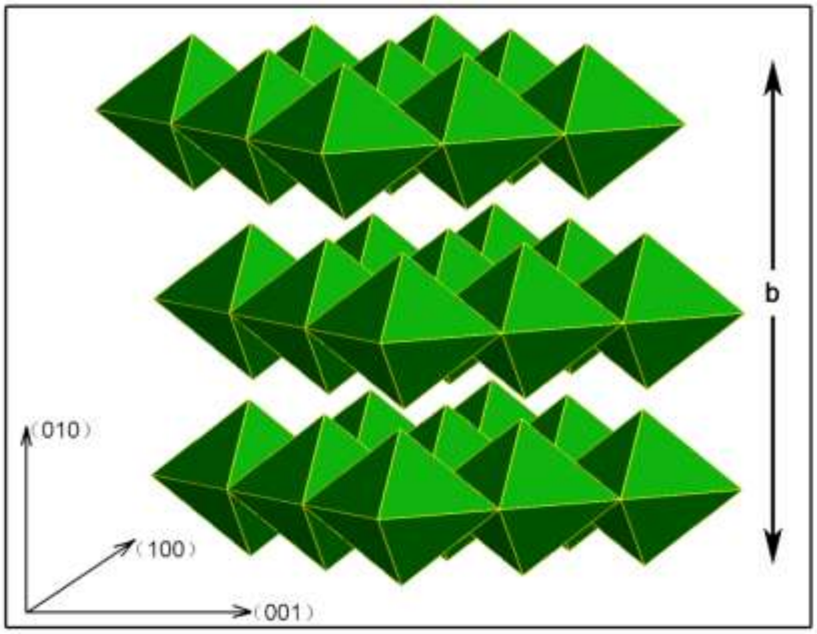

Fig. S1 The idealized polyhedral representation of α-MoO_3 structure (space group = *Pbnm*, *a*=3.963Å, *b* =13.85 Å, *c*=3.696 Å).

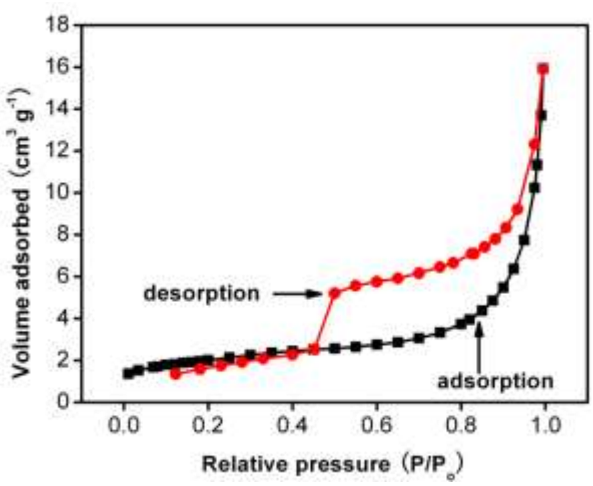

Fig. S2 Nitrogen adsorption and desorption isotherms for MG.

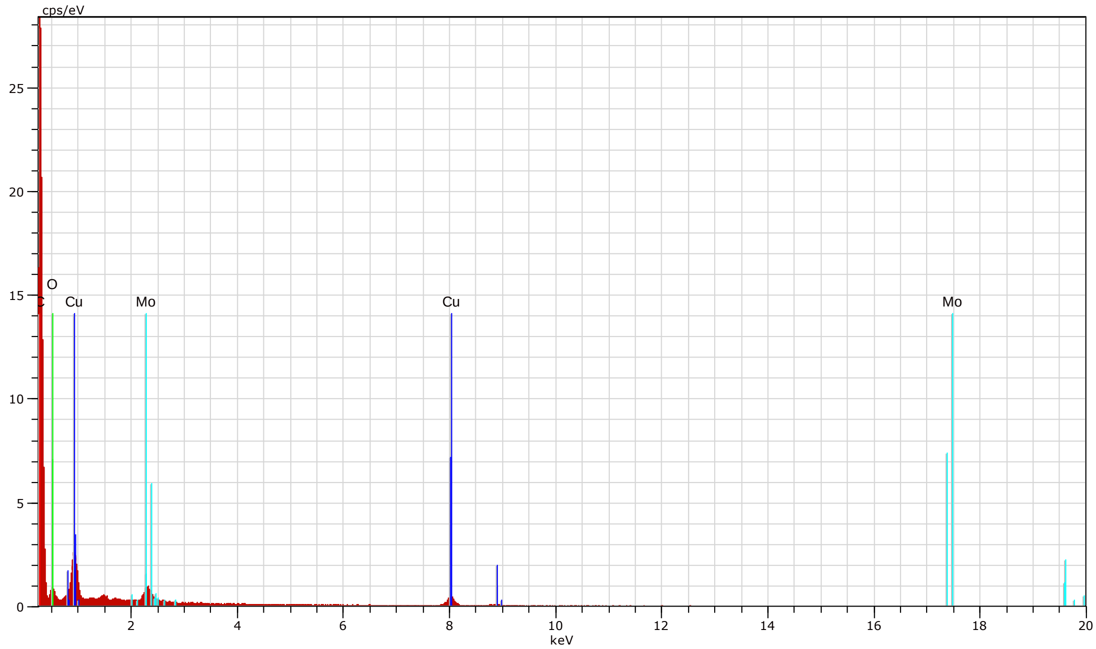

Fig. S3 Energy dispersive spectra (EDS) of MG.

Table S2 The data of EDS analysis of MG (HV: 20.0 kV, Puls th.: 3.91 kcps)

EL	AN	series	Unn. C [wt.%]	Norm. C [wt.%]	Atom. C [at.%]	Error [%]
C	6	K- series	75.36	75.36	85.38	23.5
O	8	K- series	15.02	15.02	12.78	5.3
Cu	28	K- series	6.58	6.58	1.4	0.2
Mo	42	L- series	3.04	3.04	0.43	0.1
	Total:		100	100	100	

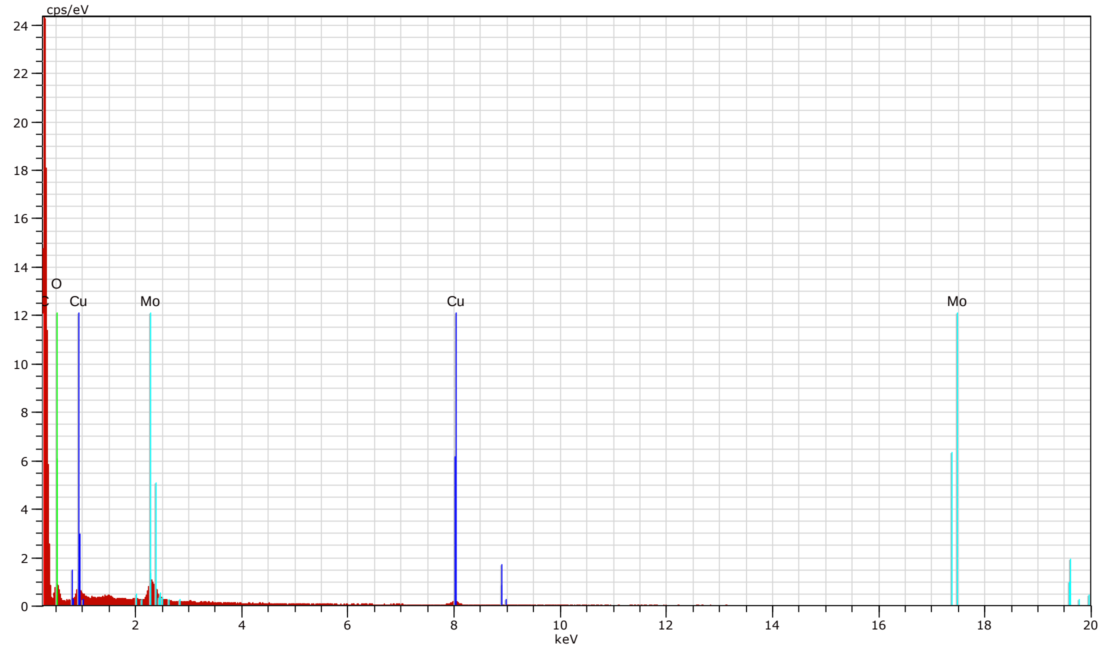

Fig. S4 Energy dispersive spectra (EDS) of TAMG.

Table S3 The data of EDS analysis of TAMG (HV: 20.0 kV, Puls th.: 3.16 kcps)

EL	AN	series	Unn. C [wt.%]	Norm. C [wt.%]	Atom. C [at.%]	Error [%]
C	6	K- series	77.92	77.92	85.38	24.3
O	8	K- series	16.70	16.70	13.74	5.9
Cu	28	K- series	2.06	2.06	0.43	0.1
Mo	42	L- series	3.32	3.34	0.46	0.2
	Total:		100	100	100	

Table S4 Capacitance values of graphene based supercapacitor.

<table>
<tr><th>Graphene material</th><th colspan="2">Discharge current density ($A\ g^{-1}$) (Specific surface area in $m^2\ g^{-1}$)</th><th>System</th><th>Specific capacitance （F/g） (electrolyte)</th></tr>
<tr><td>Chemically reuced graphene oxide[1]</td><td colspan="2">1.3 (705)</td><td rowspan="5">Two-electrode</td><td>135 (KOH)</td></tr>
<tr><td>Chemically reuced graphene oxide[2]</td><td colspan="2">1 (---)</td><td>154.1(Ionic liquid)</td></tr>
<tr><td>Chemically reuced graphene oxide[3]</td><td rowspan="4">0.1</td><td>(320)</td><td>205(KOH)</td></tr>
<tr><td>TAMG</td><td>(9.7)</td><td>86.3(KOH)</td></tr>
<tr><td>Graphene nanosheets/NiO[4]</td><td>(260)</td><td>150～220(KOH)</td></tr>
<tr><td>Solvothermal reduced graphene oxide in DMF[5]</td><td>(---)</td><td>Three-electrode</td><td>276(H_2SO_4)</td></tr>
</table>

References

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