

## Supplementary Information

### **Reduced graphene oxide: a metal-free catalyst for aerobic oxidative desulfurization**

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**The titration process:**

The titration of carbonyl groups on rGO-425 was performed as following: 200 mg phenylhydrazine and 10  $\mu$ L HCl acid (38 %) was dissolved in 10 mL  $\text{CHCl}_3$ , and then 100 mg rGO-425 was added into the solution. After stirring under  $\text{N}_2$  protection for 72 hs, the precipitate was filtered out and washed with  $\text{CHCl}_3$  in Soxhlet extractor for 20 hs to remove the physical adsorbed PH molecules. The precipitate was further washed with of  $\text{CHCl}_3$ . The precipitate is dried in vacuum at 60  $^\circ\text{C}$  overnight to give rGO-425 (PH).

The titration of carboxylic acid groups on rGO-425 was performed as following: 200 mg 2-bromo-1-phenylethanone and 100 mg rGO-425 was dissolved in 5 mL of  $\text{CHCl}_3$ . After stirring under  $\text{N}_2$  protection at room temperature in dark for 5 hs, the precipitate was filtered out and washed with of  $\text{CHCl}_3$  to remove the physical adsorbed BrPE molecules. The precipitate is dried in vacuum at 60  $^\circ\text{C}$  overnight to give rGO-425 (BrPE).

The titration of phenol groups on rGO-425 was performed as following: 500 mg benzoic anhydride and 100 mg rGO-425 was dissolved in 5 mL of  $\text{CHCl}_3$ . After stirring under  $\text{N}_2$  protection at room temperature for 24 hs, the precipitate was filtered out and washed with of  $\text{CHCl}_3$  to remove the physical adsorbed BA molecules. The precipitate is dried in vacuum at 60  $^\circ\text{C}$  overnight to give rGO-425 (BA).

Table S1. Summary of typical works dedicated to the aerobic ODS reaction

Entry	Catalyst	Reaction Temperature(°C)	Reaction rate* (h <sup>-1</sup> )
1	$[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18} \cdot 3H_2O$	80	0.49 <sup>1</sup>
2	$[C_8H_{17}N(CH_3)_3]_5H_4PV_{14}O_{42}$	100	0.48 <sup>2</sup>
3	$[(C_{18}H_{37})_2N(CH_3)_2]_5[IMo_6O_{24}]$	100	1.25 <sup>3</sup>
4	Ce–Mo–O	100	0.09 <sup>4</sup>
5	Cu NPs/g-BN	120	0.14 <sup>5</sup>
5	$Cr_3F(H_2O)_2O[(O_2C)-C_6H_4-(CO_2)]_3 \cdot nH_2O$	140	0.51 <sup>6</sup>
6	CNT	140	5.90 <sup>7</sup>
7	rGO-425(this work)	140	7.19
9	BN	150	0.19 <sup>8</sup>

\*Reaction rate are normalized by catalyst weight.

To determine the metal content in the rGO, inductively coupled plasma atomic emission spectroscopy (ICP-AES) test was employed. 20 mg rGO and 20 g concentrated nitric acid was mixed into a hydrothermal autoclave and then maintained at 200 °C for 36 h. The obtained transparent liquid was diluted to 25 mL by deionized water. And the results were tabulated in Table S2. Moreover, in order to evaluate the impact of trace amount of Fe (which may exist in natural graphite) and Mn (which could be introduced during the process of catalyst preparation) in the rGO on the catalytic performance, two catalysts with extra loadings of Fe and Mn (that is, FeOx/rGO and MnOx/rGO containing 3 wt% Fe and Mn, respectively) were prepared by excessive wetness impregnant method. The samples were prepared by suspending 100 mg of rGO in 100 mL water and addition of 13.22 mg Fe(NO<sub>3</sub>)<sub>3</sub> (98%) and 31.35 mg Mn(NO<sub>3</sub>)<sub>2</sub> solution (50% w/w, Alfa) under magnetic stirring at room temperature, respectively. The suspension is stirred for 6 h, concentrated by rotary evaporator and then dried in an oven at 120 °C. The resulting powder was heated for 2 h at 500 °C under nitrogen stream before using the material as catalyst. The catalytic activities of FeOx/rGO and MnOx/rGO over aerobic oxidation of DBT are summarized in Table S3.

## Tables

Table S2. Metal contents of rGO by ICP-MS analysis.

Catalyst	Mn (wt%)	Fe (wt%)	Zn (wt%)	Cu (wt%)
rGO	0.025	0.0125	N.D	N.D.

Table S3. Catalytic activity of different catalysts over aerobic oxidation of DBT.

Entry	Catalyst	Conversion(%)
1	rGO	65.3
2	3wt%FeOx/rGO	68.3
3	3wt%MnOx/rGO	66.7

Reaction conditions: m (DBT) = 57.46 mg, O<sub>2</sub> = 200 mL/min, m (catalyst) = 5 mg,

T = 140 °C, time = 2h.

Table S4. BET surface areas of thermal treated rGO and titrated rGO samples.

Samples	BET surface area (m <sup>2</sup> /g)
rGO	492
rGO-325	506
rGO-375	523
rGO-425	549
rGO-425-PH	416
rGO-425-BrPE	468
rGO-425-BA	518
rGO-H <sub>2</sub> -800	491

## Figures

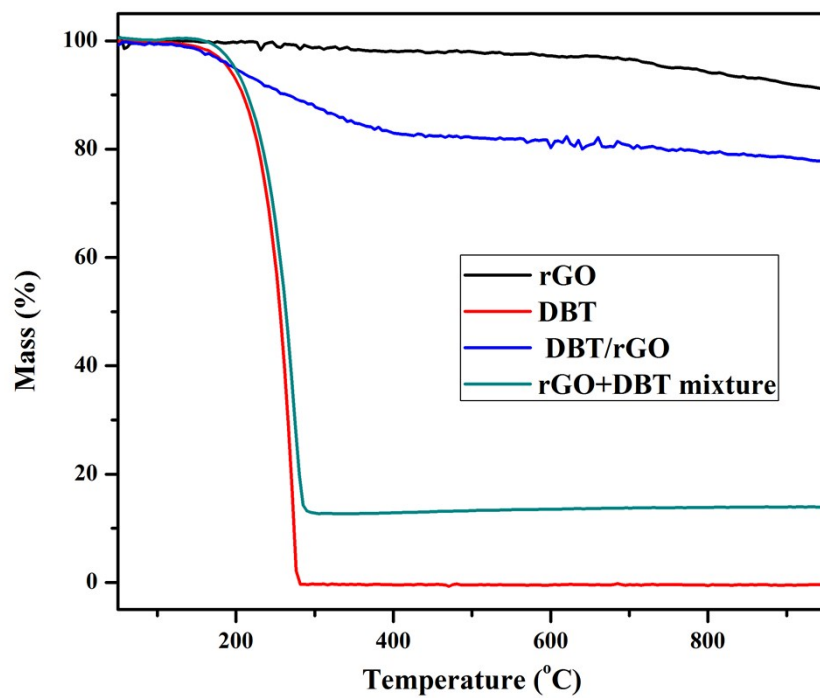


Figure S1. TG curves of rGO, DBT , rGO with adsorbed DBT and simple mixture of DBT and rGO.

The GC-MS analysis was carried out to confirm the oxidized products of the sulfur-containing compounds in the fuel. The details of the experiment are as follows.

After the reaction, the solid (catalyst and products) was separated from the reaction system by centrifugation. And then the obtained solid were washed by methanol to separate the catalyst and products. After the washing step, the methanol containing products was collected for GC-MS analysis. The GC results showed in the insert pictures of Fig. S2 suggest that there are two signals in each picture. The first peaks all attributes to the reactants remained in the reaction system and the second signals all belong to the corresponding sulfone according to the MS results. Based on these results, it is proved that the sole products after the ODS are sulfones. Hence, clean oil can be obtained by the catalytic system we reported in this work since the oxidized products are less dissoluble in the mother liquid.



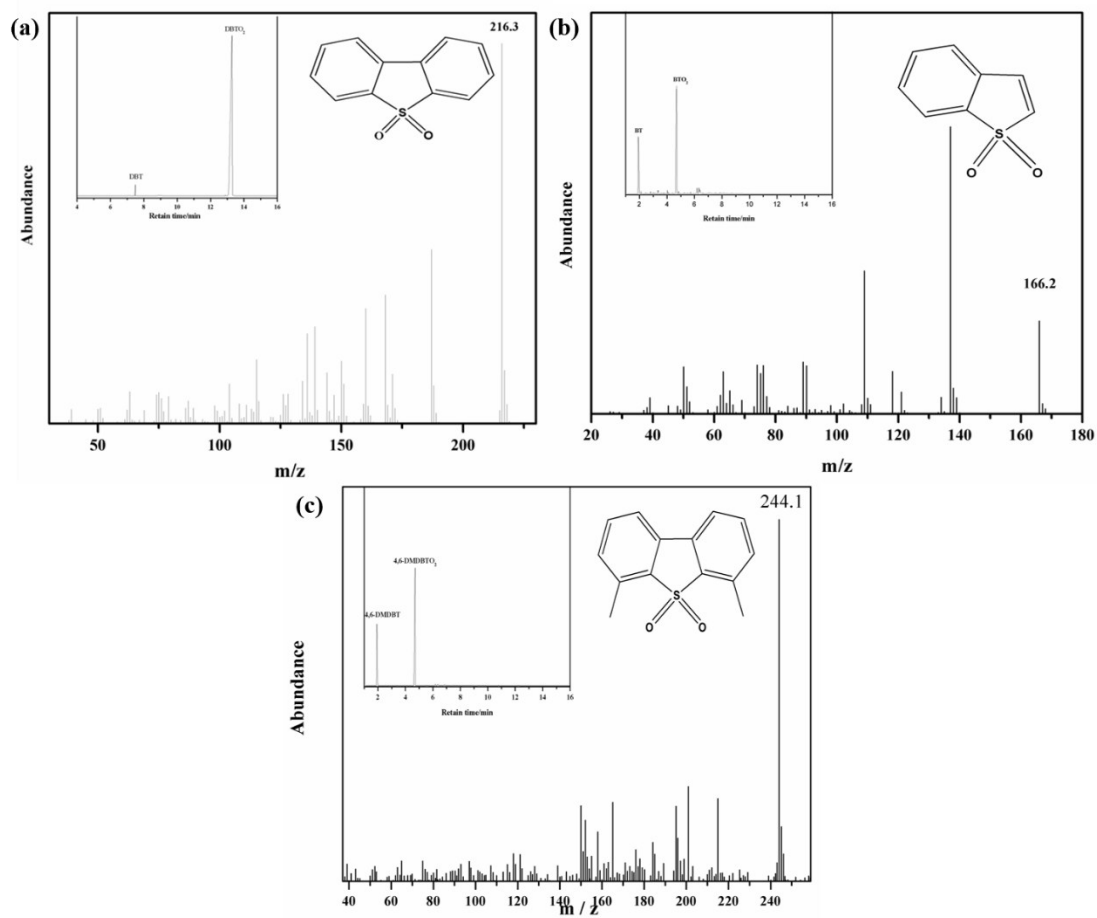


Figure S2. GC-MS analysis of the organic phase extracting from the catalyst after the oxidation of DBT (a), BT (b) and 4, 6-DMDBT (c) reaction.

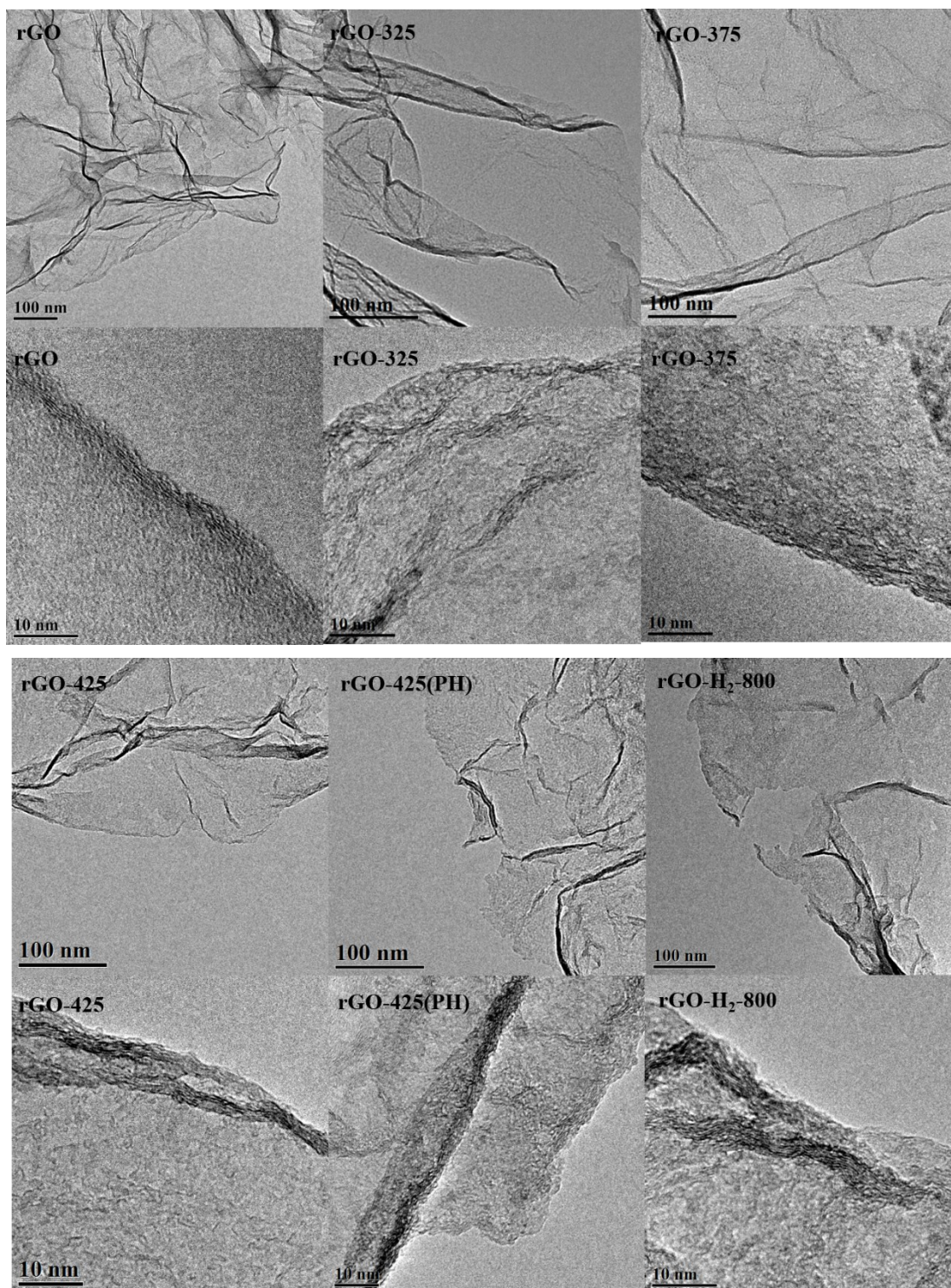


Figure S3. TEM and HRTEM images of rGO and treated rGO materials.

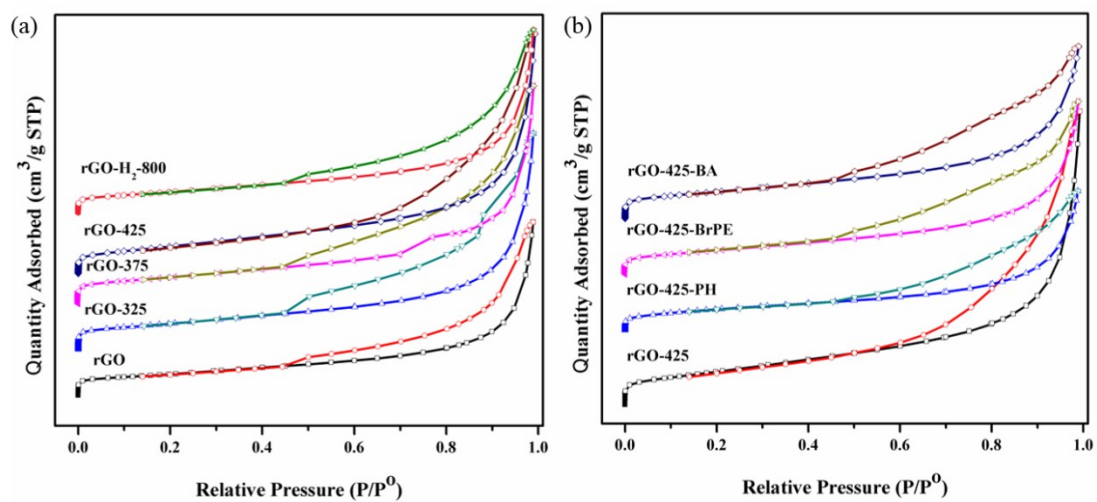


Figure S4. Nitrogen adsorption-desorption isotherm of thermal treated rGO (a) and titrated rGO (b) samples.

To calculate the initial reaction rate ( $r_{\text{initial}}$ ), the reaction liquid was collected with different interval time to carefully control the conversion at a low level and analyzed immediately by GC. Due to the low conversion inside the kinetic range, the initial reaction of the ODS reaction can be approximately regarded as a constant. Therefore, the initial reaction rate derived from the plot of converted DBT (ppm) against reaction time (min).

$$r_{\text{initial}} = \frac{\text{converted DBT}}{\text{reaction time}} = \frac{C_0 - C_t}{\text{reaction time}} \text{ ppm/min}$$

( $C_0$  indicates the initial DBT concentration,  $C_t$  indicates the DBT concentration at a given reaction time)

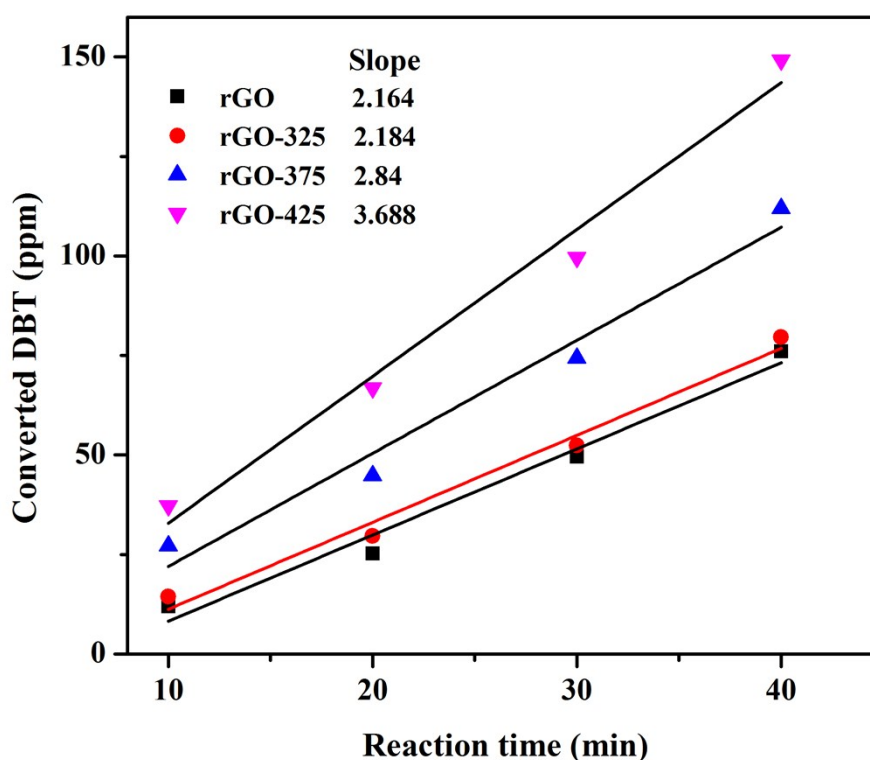


Figure S5. A plot of converted amount of DBT versus reaction time.

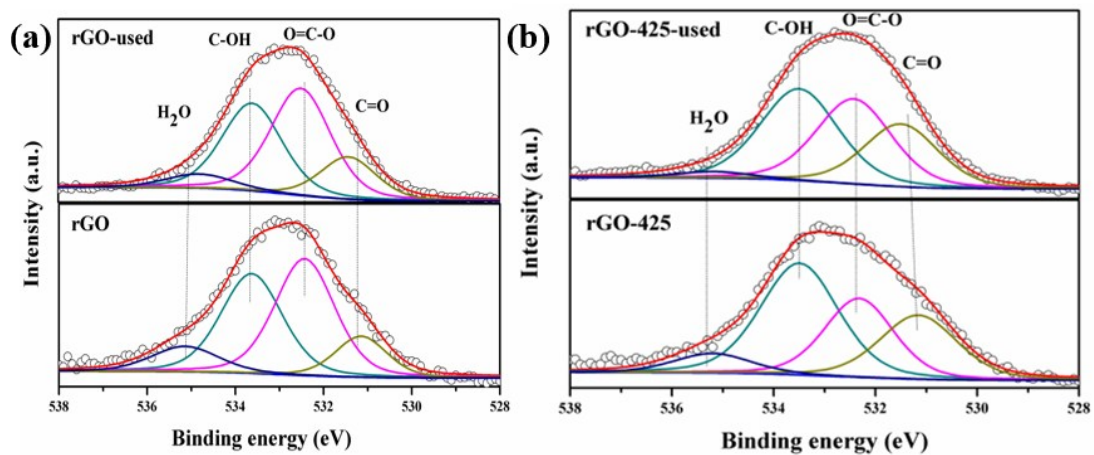


Figure S6. The O1s XPS spectrum of rGO (a) and rGO-425 (b) before and after reaction.

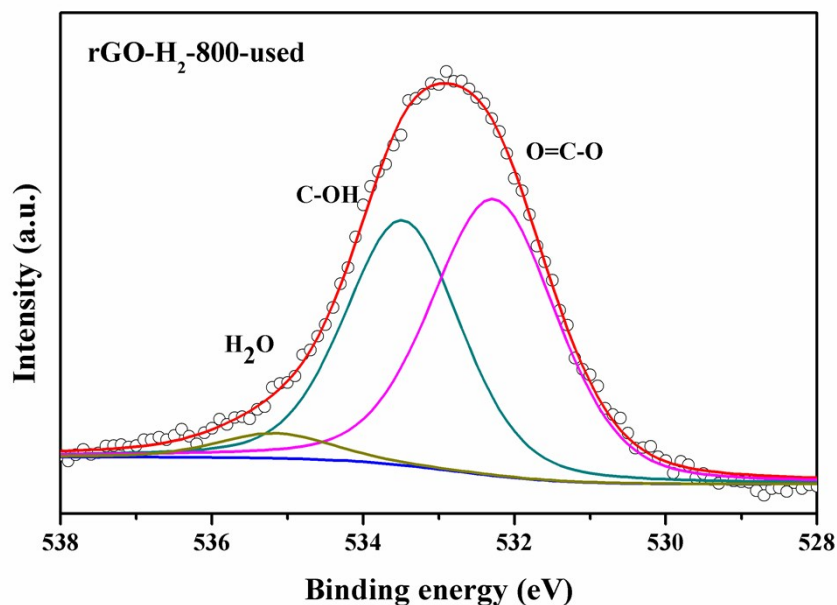


Figure S7. The O1s XPS spectrum of used rGO-H<sub>2</sub>-800.

## References

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