

## Electronic Supplementary Information

# A Novel Composite of $W_{18}O_{49}$ Nanorods on Reduced Graphene Oxide Sheets Based on *in situ* Synthesis and Catalytic Performance for Oxygen Reduction Reaction

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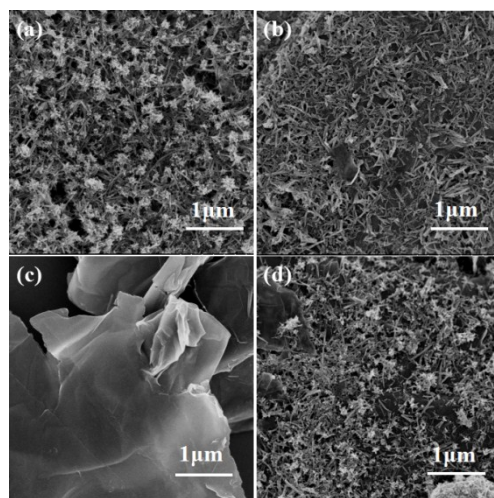
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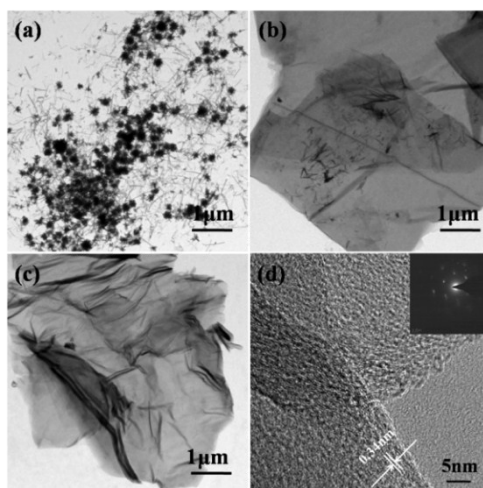
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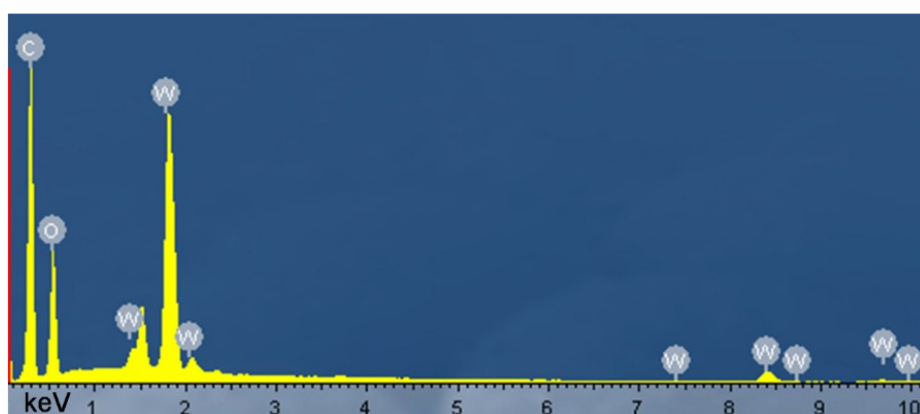
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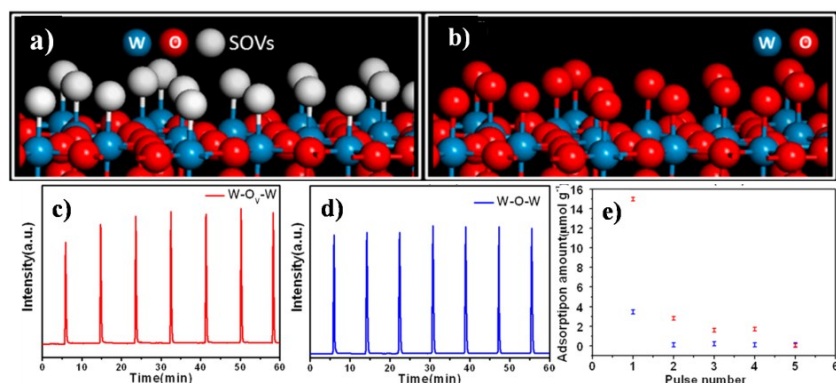
**Figure S1** Low-magnification SEM images of (a)  $W_{18}O_{49}$ , (b)  $W_{18}O_{49}$ -rGO, (c) rGO, and (d) mixed  $W_{18}O_{49}$ +rGO .



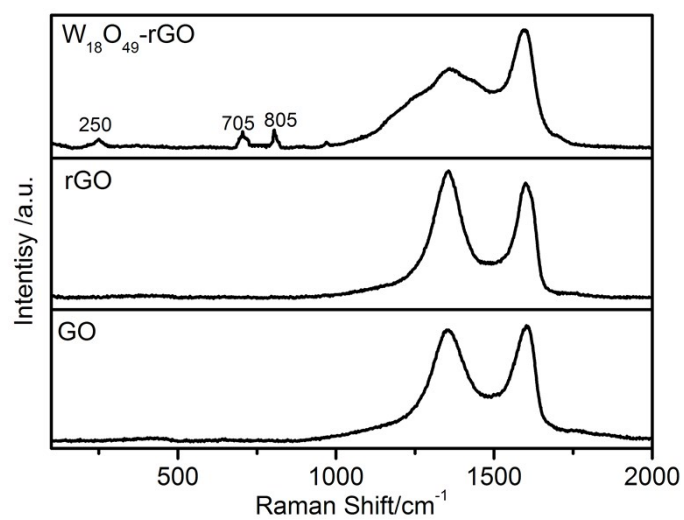
**Figure S2** Low-magnification TEM images of (a)  $W_{18}O_{49}$ , (b)  $W_{18}O_{49}$ -rGO, and (c) rGO. (d) HRTEM image of rGO. The inset in (d) shows the corresponding SAED pattern.



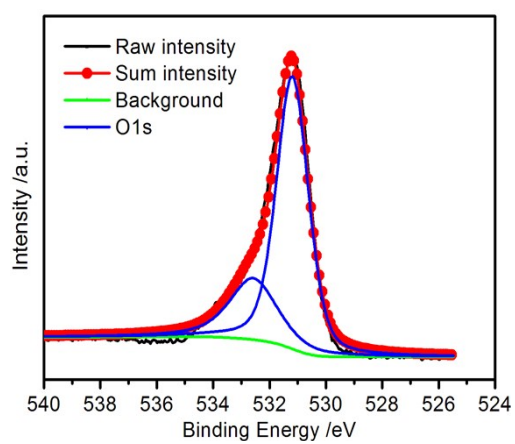
**Figure S3** EDX spectrum of the  $W_{18}O_{49}$ -rGO sample.



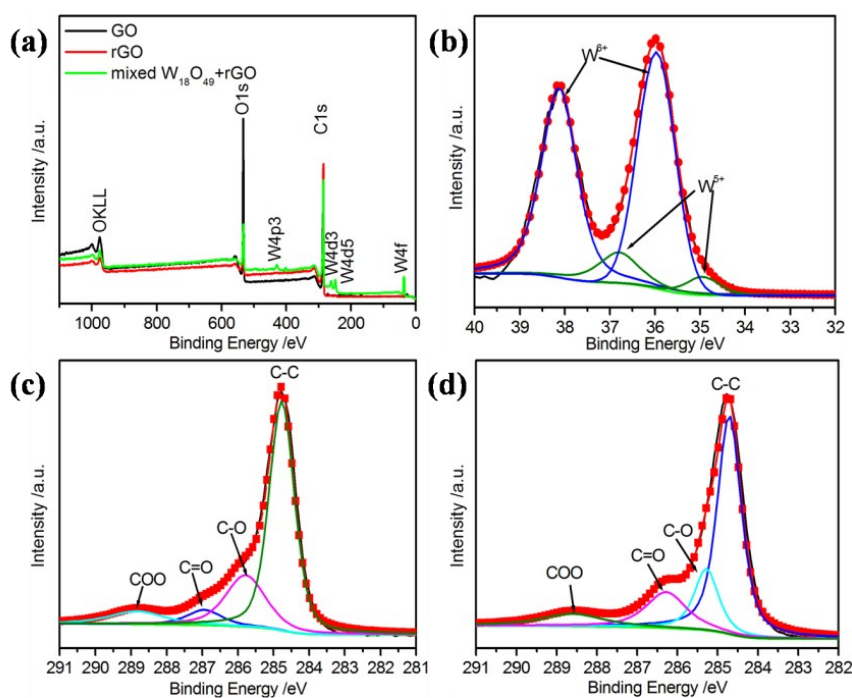
**Figure S4** (a, b) Schematic diagrams of the surface of  $W_{18}O_{49}$  with and without surface oxygen vacancies, respectively. (c, d) Oxygen pulse chemisorption of  $W-O_V-W$  ( $W_{18}O_{49}$ ) and  $W-O-W$  ( $WO_3$ ), respectively. (e) Adsorption amount-pulse number curves of  $W-O_V-W$  (red) and  $W-O-W$  (blue), which is measured by thermal conductivity detector.<sup>1</sup>(For review only)



**Figure S5** Raman spectrum of W<sub>18</sub>O<sub>49</sub>-rGO composite catalyst.



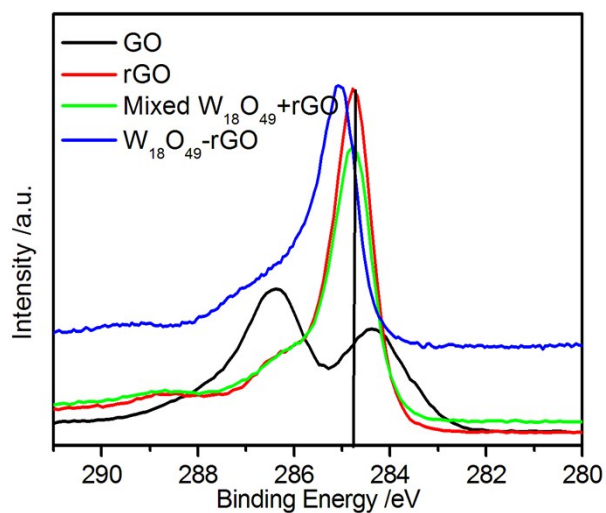
**Figure S6** O 1s core-level and corresponding deconvoluted spectra for W<sub>18</sub>O<sub>49</sub>-rGO composite.



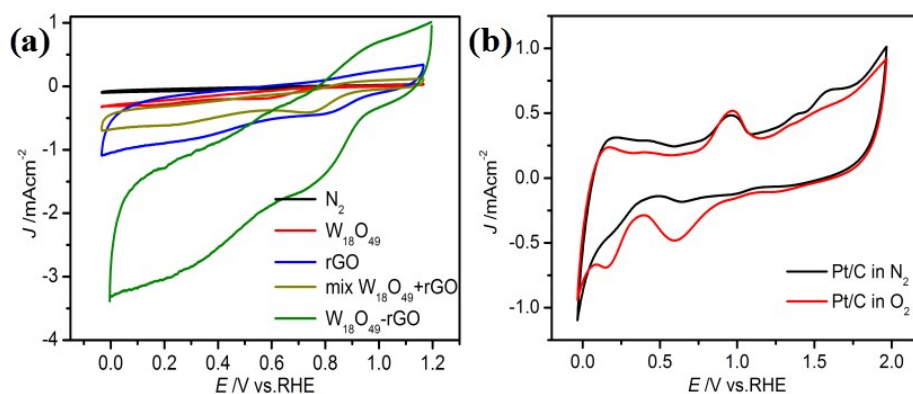
**Figure S7** (a) XPS spectra of GO, rGO, and mixed  $W_{18}O_{49}$ +rGO; (b) high resolution W 4f spectrum and corresponding deconvoluted spectra of mixed  $W_{18}O_{49}$ +rGO. (c) C 1s core-level and corresponding deconvoluted spectra of mixed  $W_{18}O_{49}$ +rGO; (d) C 1s core-level and corresponding deconvoluted spectra of rGO.

**Table S1** Binding energy and percentages of different bindings calculated from the deconvoluted XPS spectra of C 1s peak

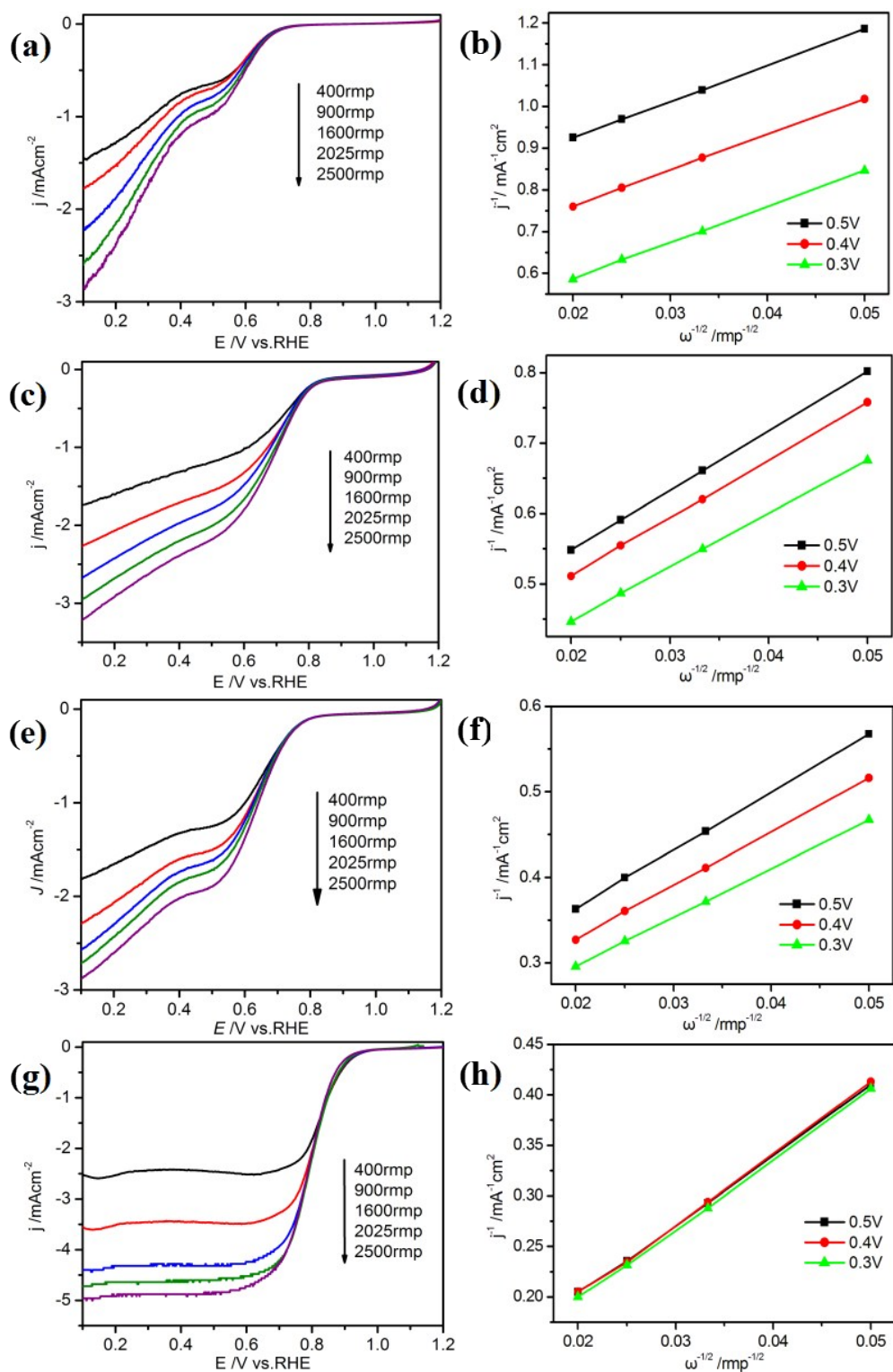
| Binding | GO             |            | rGO            |            | Mixed $W_{18}O_{49}$ +rGO |            | $W_{18}O_{49}$ -rGO |            |
|---------|----------------|------------|----------------|------------|---------------------------|------------|---------------------|------------|
|         | Binding energy | percentage | Binding energy | percentage | Binding energy            | percentage | Binding energy      | percentage |
| C-C     | 284.7          | 32.9%      | 284.7          | 57.8%      | 284.8                     | 62.4%      | 284.8               | 54.7%      |
| C-O     | 286.8          | 53.2%      | 285.3          | 16.7%      | 285.4                     | 23.0%      | 285.4               | 29.3%      |
| C=O     | 287.9          | 10.9%      | 286.3          | 16.4%      | 286.8                     | 6.2%       | 286.7               | 10.3%      |
| COO     | 289.0          | 3.0%       | 288.6          | 9.1%       | 288.8                     | 8.4%       | 289.0               | 5.7%       |



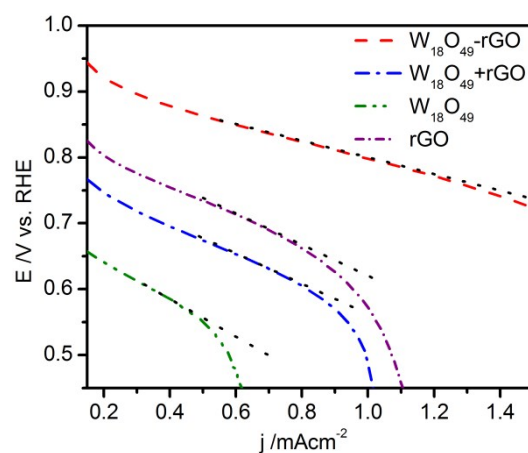
**Figure S8** Comparison of core-level spectra of C 1s for GO, rGO, Mixed  $W_{18}O_{49}$ +rGO, and  $W_{18}O_{49}$ -rGO composite.



**Figure S9** CVs of (a)  $W_{18}O_{49}$ , rGO,  $W_{18}O_{49}$ +rGO,  $W_{18}O_{49}$ -rGO, (b) Pt/C in  $N_2$ - and  $O_2$ -saturated 0.1M KOH solution at a scan rate of  $10\text{ mV}\cdot\text{s}^{-1}$ .



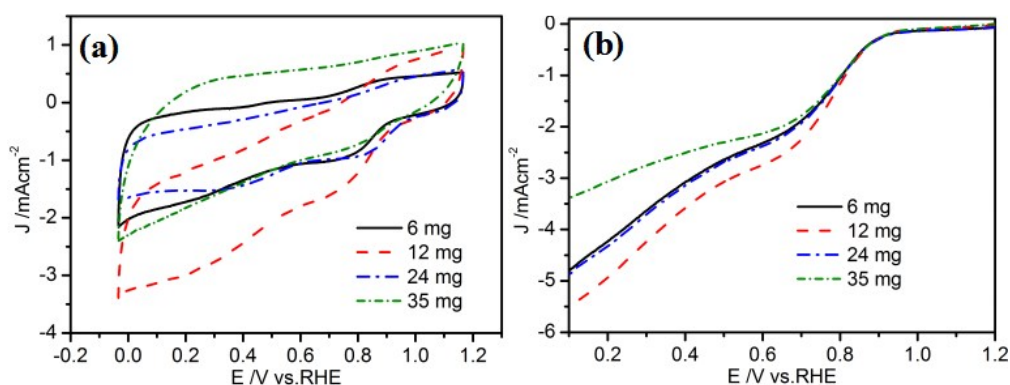
**Figure S10** LSVs of (a)  $W_{18}O_{49}$ , (c) rGO, (e)  $W_{18}O_{49} + \text{rGO}$ , (g) Pt/C in  $O_2$ -saturated 0.1M KOH at a scan rate of  $10 \text{ mV} \cdot \text{s}^{-1}$  at different RDE rotation rates and the calculated K-L plots of the ORR from (b)  $W_{18}O_{49}$ , (d) rGO, (f)  $W_{18}O_{49} + \text{rGO}$ , (h) Pt/C.



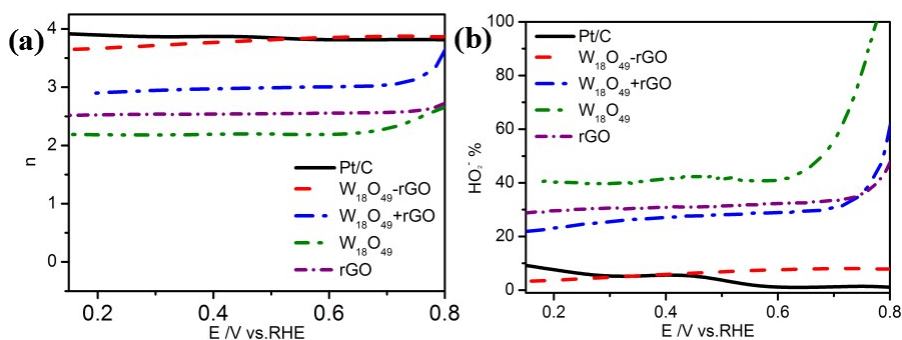
**Figure S11** The Tafel plots derived from Figure 4a in the low-current region as the follow equation

$$J_K = \frac{JJ_D}{J_D - J}$$

where  $J_K$  is the kinetic current density,  $J_D$  the limiting current density and  $J$  the measured current density.

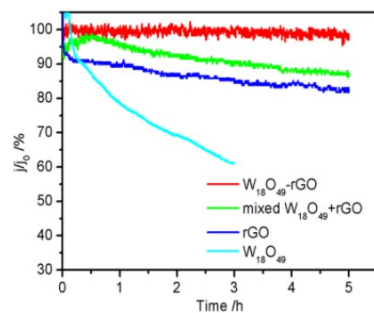


**Figure S12** The effect of catalytic activity for rGO content in composite catalyst



**Figure S13** (a) The electron transfer number and (b) percentage of peroxide of  $W_{18}O_{49}$ , rGO, mixed  $W_{18}O_{49}+rGO$ ,  $W_{18}O_{49}-rGO$ , and Pt/C obtained from the rotating ring-disk electrode measurements in  $O_2$ -saturated 0.1 M KOH at a sweep rate of  $10 \text{ mV} \cdot \text{s}^{-1}$  and a rotation rate of 1600 rpm.





**Figure S14** Chronoamperometric response ( $i-t$ ) of  $W_{18}O_{49}$ -rGO, mixed  $W_{18}O_{49}$ +rGO, rGO, and  $W_{18}O_{49}$ . The tests were conducted in  $O_2$ -saturated 0.1 M KOH solution at 0.7 V.

## Reference

- [1] H. W. Zhou, Y. T. Shi, Q. S. Dong, J. Lin, A. Q. Wang, T. L. Ma, *J. Phys. Chem. C*, 2014, 118, 20100.