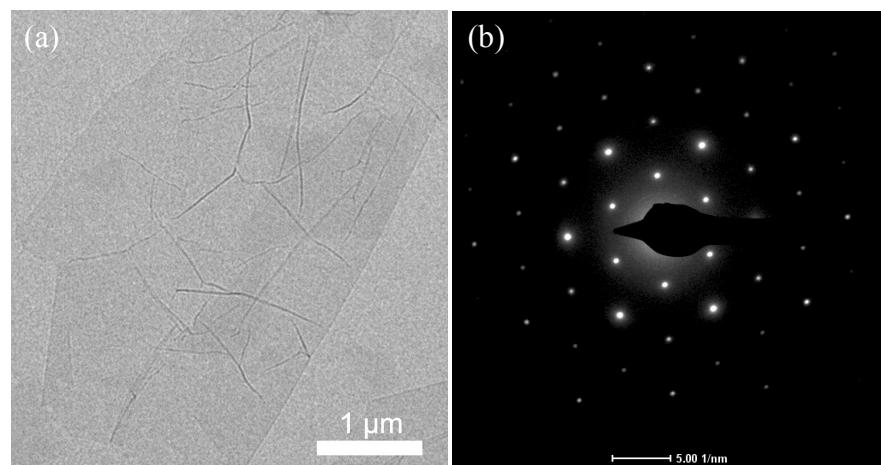


## Supporting Information

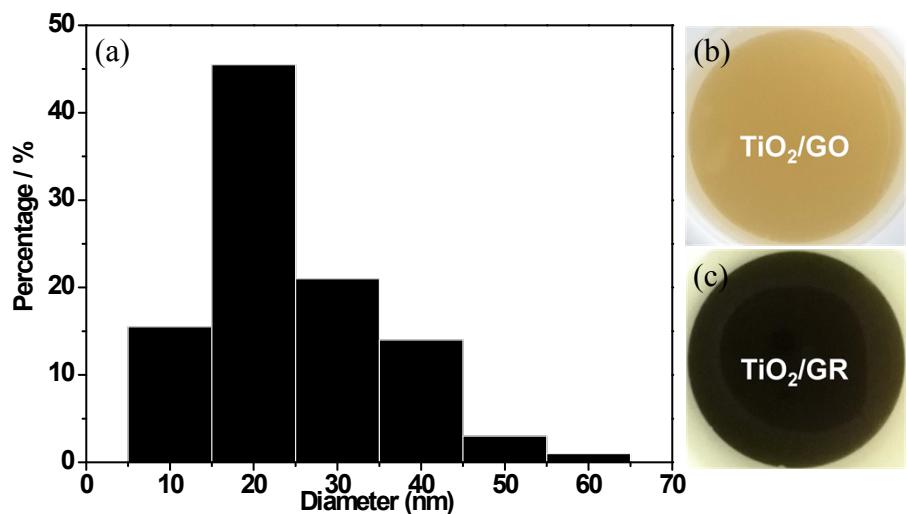
### Effect of annealing temperature and element composition of the titanium dioxide/graphene/hemin catalysts for oxygen reduction reaction

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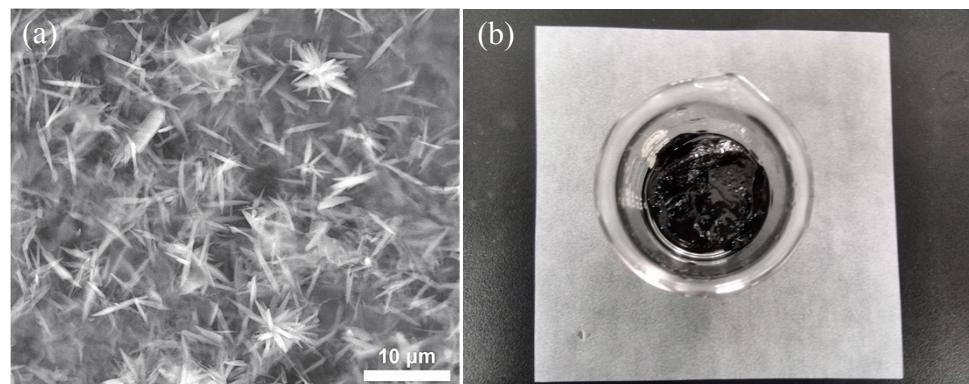
Jiangsu Province Hi-Tech Key Laboratory for Bio-medical Research, School of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China. Fax: +86-25-52090618; Tel: +86-25-52090613; E-mail address: liusq@seu.edu.cn; yuanjian.zhang@seu.edu.cn



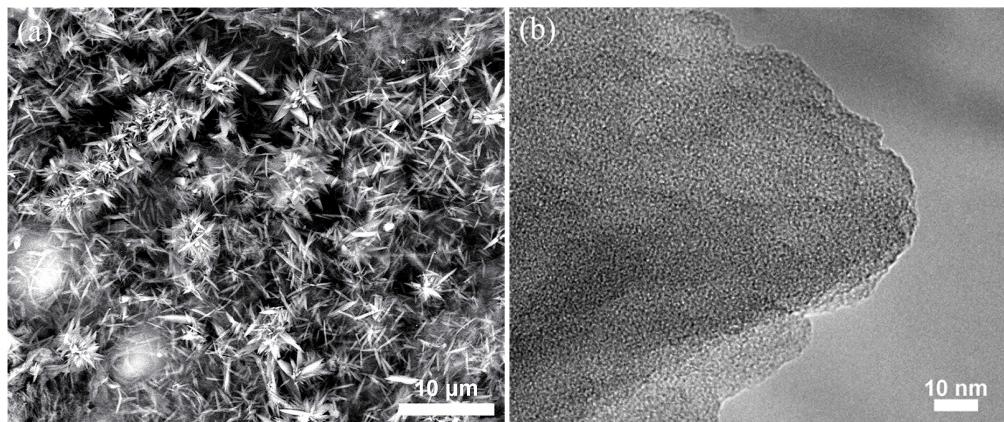
**Fig. S1** Typical TEM image (a) and SAED pattern (b) of the graphene.



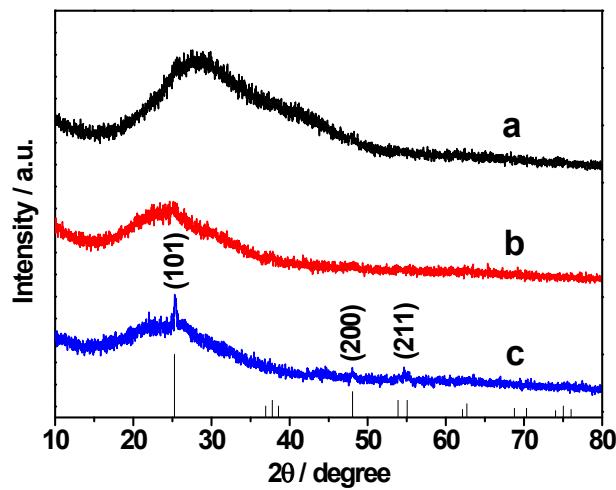
**Fig. S2** (a) Particle size distribution of the as-prepared  $\text{TiO}_2$  was investigated in the  $\text{TiO}_2/\text{GR}$  hybrids. (b)  $\text{TiO}_2$ -graphene oxide before solvothermal reaction. (c)  $\text{TiO}_2$ -reduced graphene obtained after solvothermal reaction.



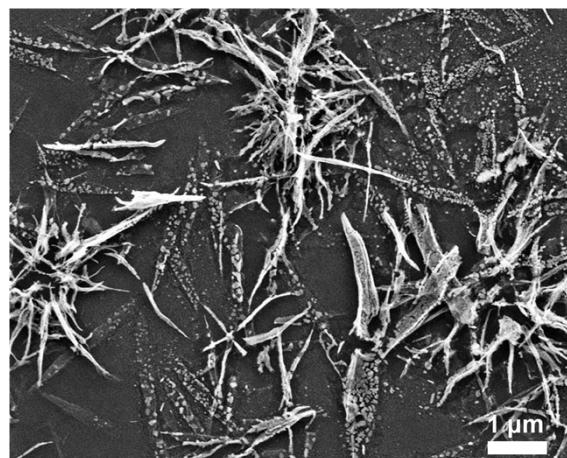
**Fig. S3** SEM and photograph images of the as-prepared  $\text{TiO}_2/\text{Gr}/\text{Hem}$  samples with different ratio of hemin and  $\text{TiO}_2/\text{Gr}$ : (a) 3/1, and (b) 1/3.



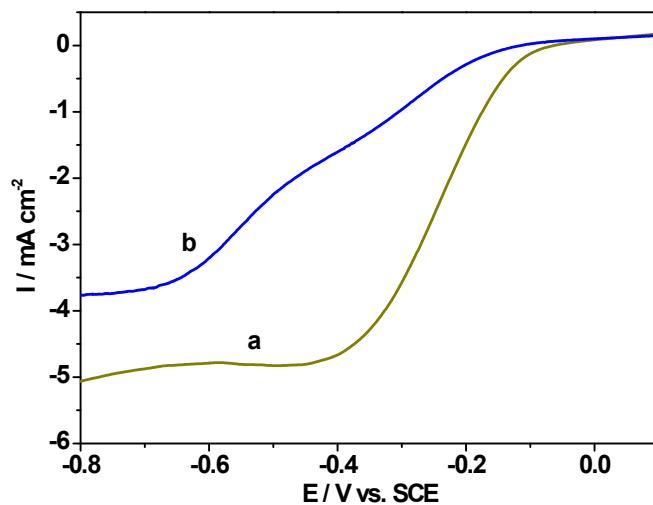
**Fig. S4** (a) SEM image of the as-prepared TiO<sub>2</sub>/Gr/Hem samples. (b) HRTEM image of the as-prepared TiO<sub>2</sub>/Gr/Hem samples.



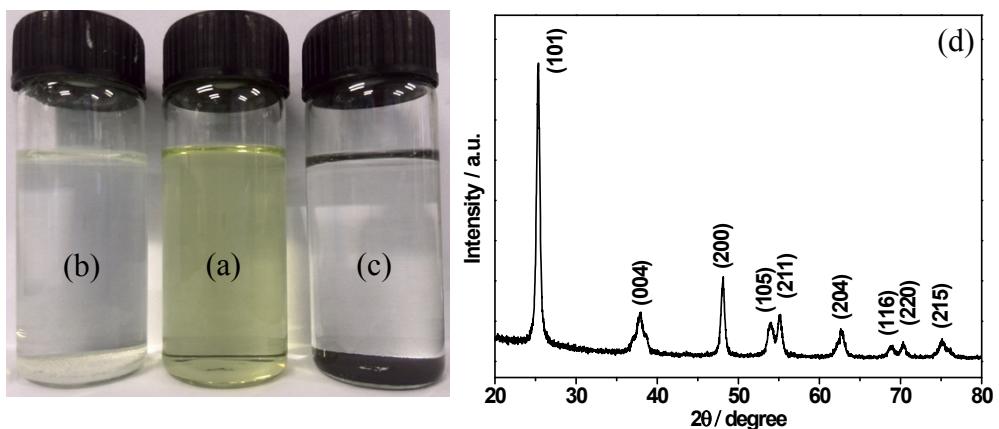
**Fig. S5** XRD patterns of the as-prepared (a) TiO<sub>2</sub>/Gr, (b) TiO<sub>2</sub>/Gr/Hem, and (c) TiO<sub>2</sub>/Gr/Hem-700 °C. The standard pattern derived from the anatase TiO<sub>2</sub> (JCPDS card No. 21-1272). It can be seen that the anatase TiO<sub>2</sub> in the TiO<sub>2</sub>/Gr/Hem was obtained after the annealing temperature at 700 °C.



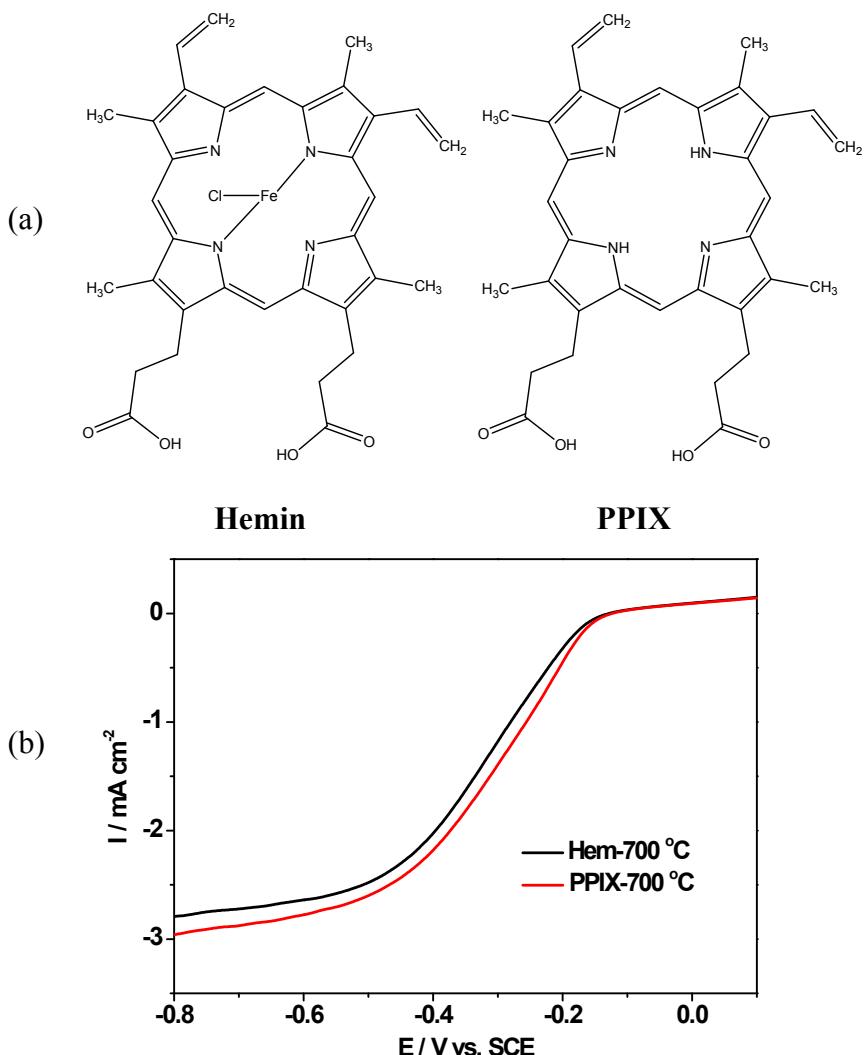
**Fig. S6** SEM images of the as-obtained  $\text{TiO}_2/\text{Gr}/\text{Hem}$ -700 °C.



**Fig. S7** LSV curves of the (a)  $\text{TiO}_2/\text{Gr}/\text{Hem}$ -700 °C materials (b)  $\text{TiO}_2$ , graphene, and hemin were directly mixed and annealed at 700 °C. Scan rate, 10 mV s<sup>-1</sup>; rotation rate, 1600 rpm.



**Fig. S8** (a) The amorphous  $\text{TiO}_2$  can be dissolved in hydrochloric acid. (b) The obtained anatase  $\text{TiO}_2$  after the annealing temperature at  $700\text{ }^\circ\text{C}$ , it cannot be dissolved in hydrochloric acid. (c) The  $\text{TiO}_2/\text{Gr}-700\text{ }^\circ\text{C}$  also cannot be dissolved in hydrochloric acid. (d) XRD pattern of the obtained anatase  $\text{TiO}_2$  after the annealing temperature at  $700\text{ }^\circ\text{C}$ .



**Fig. S9** (a) Structural diagrams of the hemin and PPIX. (b) LSV curves of Hem-700 °C (black line) and PPIX-700 °C (red line) in O<sub>2</sub>-saturated 0.1 M KOH. Scan rate, 10 mV s<sup>-1</sup>; rotation rate, 1600 rpm.