

Supplementary information

The effect of tunable graphene oxide sheet size on the structures and catalytic properties of three-dimensional reduced graphene oxide sponge

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Experimental details

Materials

32, 325 and 1200 mesh natural graphite flakes were obtained from Qingdao Jinrilai Graphite Co., Ltd. Concentrated H₂SO₄ (98 %), KMnO₄, P₂O₅, H₂O₂ (30 %) solution, K₂S₂O₈, H₂PtCl₆·6H₂O, NaBH₄, and ascorbic acid were purchased from Aladdin Chemical Reagent Co., Ltd. and used as received.

The preparation and size fractionation of GOSs

As shown in figure 1, we prepared GOSs from different natural graphite flakes with 32, 325 and 1200 mesh. The process included three steps: oxidization, size fractionation, and exfoliation.

In the first step, LGO sheets was prepared from 32 mesh natural graphite flakes according to previously reported method¹ with average lateral size of 500 μm. This process included three steps: expanded graphite, pre-oxidized graphite, and GOSs. Firstly, natural graphite flakes (5 g), 98% sulfuric acid (150 mL) and fuming nitric acid (50 mL) were step wisely added into a 500 mL flask. The mixture was kept at room temperature and stirred for 24h. The mixture was then poured slowly into 1 L water to collect the solid by filtration. The solid was washed using water for three times. After drying at 50 °C for 24 h, the graphite intercalation compounds were obtained. The dry

graphite intercalation compounds powder was thermally expanded at 1000 °C for 10 s to get expanded graphite. Secondly, 5 g EG powder, 300 mL sulfuric acid, 4.2 g $K_2S_2O_8$ and 6.2 g P_2O_5 were added successively into a 500 mL flask and the mixture was kept at 80°C for 5 h. After cooling to room temperature, the mixture was diluted and washed with 2L water by vacuum-filtered. The solid was dried in air at room temperature for 24h to get preoxidized graphite. Finally, the preoxidized expanded graphite was added into 200 mL concentrated H_2SO_4 (0°C), and then 15 g $KMnO_4$ was added slowly under continuous stirring. After the introduction of $KMnO_4$, the mixture was heated to 35 °C and stirred for 2 h. The mixture was then diluted with 2L water, followed by dropwise addition of 10 mL 30% H_2O_2 . The smaller GOSs (325 and 1200 mesh) were synthesized without expanding, because it was oxidized easily.

In the second step, after the process of oxidation, the mixture was repeatedly washed with HCl solution (1:10) and water. During the process of acid cleaning, the GO dispersion was centrifuged at 1100 rpm for 3 min. Then the dispersion was separated into two portions: large and small lateral dimensions by low speed centrifugation. Larger GO (32 and 325 mesh) left the larger part, while the smaller portion was left from 1200 mesh. The low speed centrifugation process was repeated three times for narrowing the size distribution. Then, it was purified by dialysis for one week using a dialysis membrane with a molecular weight cut off of 8000 to 10000 $g\ mol^{-1}$ which removed the remaining acid and metal species.

In the third step, graphite oxide was exfoliated by the freeze–thaw method². The tube of GO was soaked in a liquid nitrogen bath and kept for approximately 30 s. After freezing the mixture completely, the tube was soaked in a thermostated bath at 333 K for 5 min. Then, the mixture was centrifuged at 3000 rpm for 5 min, and the supernatant solution was characterized by UV spectrum. This freeze–thaw cycle was repeated four times. In total, this exfoliation process takes <1 h. The GO solution was collected as large graphene oxide (LGO), medium graphene oxide (MGO) and small graphene oxide (SGO) from graphite 32, 325 and 1200 mesh.

The preparation of GO sponge and GO paper

GO sponge were prepared by lyophilization. 10g GO dispersions (2 mg g^{-1}) with SGO, MGO, and LGO respectively were put in the glass bottle through freeze-drying process. GO sponge was obtained. GO papers were prepared by vacuum filtration of 0.1 mg g^{-1} GO dispersions of SGO, MGO, and LGO solution. The thickness of each GO paper was controlled by adjusting the content

of GO suspension (4g). After filtration, the paper was peeled off from the filter membrane and dried at ambient conditions overnight.

The preparation of 3D rGO sponge

3D rGO sponge were prepared by mild chemical reduction³. The ascorbic acid was added in GO dispersions (2 mg g⁻¹) of SGO, MGO, and LGO respectively. The ratio of ascorbic acid to GO was triple. For obtaining the variation of microstructure from GOSs to 3D rGO sponge, a special method was used to prepare 3D rGO sponge materials. The mixture was placed in boiling water bath for 10 min to obtain a mesomorphic GO dispersion. The vial was then immersed in a dry ice bath to freeze for 0.5 h. After being thawed at room temperature, the vial was placed in a boiling water bath to further reduce GO for 30 min. The 3D rGO sponge was obtained⁴. Clear pore structure characterized by SEM was prepared which indicated the formation of structure from GOSs to 3D rGO sponge.

The preparation of Pt-rGO composite catalyst

The chloroplatinic acid (10%) and five-fold ascorbic acid compared with GO were added to the GO dispersions. Afterwards, the mixture was stirred for 3 hours, and then maintained at 100 °C for 2h. After being cooled to the room temperature, the Pt-rGO composite hydrogel was formed with a height of 1.2cm and the diameter of 1 cm. Then the catalyst was washed by large amount of ethanol and water to remove the residual ascorbic acid and other by-products. In order to investigate the catalytic activity of Pt- rGO composite, 6mL 4-nitrophenol (0.033mM) and the freshly prepared 14mL NaBH₄ (0.4mM) was mixed homogeneously at room temperature. Then the catalyst was added into the mixture. The reduction progress was monitored with UV-vis spectroscopy.

Notes and references

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