Electronic Supplementary Information

An effective strategy to small-sized and high-dispersed palladium nanoparticles supported on graphene with excellent performance for formic acid oxidation

Jun Yang, Chungui Tian, Lei Wang and Honggang Fu*

Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of the People's Republic of China, Heilongjiang University, Harbin 150080 P. R. China.

Tel.: +86 451-86608458; Fax: +86 451-86673647

E-mail: fuhg@vip.sina.com
Preparation of graphene oxide (GO)

GO was synthesized from expandable graphite according to a modified Hummers method. First, commercial expandable graphite was filtrated with an appropriate boult. Afterwards, expandable graphite was ground with sodium chloride, then washing away sodium chloride with water. The expandable graphite obtained was dried at 70 °C for 12 h. The dry solid was infused in 23 mL concentrated sulfuric acid in a beaker and stirred at room temperature for 24 h. 0.5 g of sodium nitrite was added into the suspension. After sodium nitrite entirely dissolved, 3 g of potassium permanganate was added into the beaker under an ice bath. The solution was maintained for 30 minutes at about 60 °C under a water bath. Then, 10 mL of distilled water was added into the solution. 5 minutes later, 100 mL of distilled water was added into the beaker and succeeding 10 mL of 30 % H₂O₂ was added into the reaction system. The yellow suspension obtained was filtrated and washed with diluted HCl solution, then washed repeatedly with distilled water finally. The obtained solid was dried at 70 °C for 48 h in oven.

Fig. S1 TEM of (a) Pd/GN2, (b) Pd/GN1, and the size distribution of Pd NPs in the Pd/GN2 and Pd/GN1 catalysts.
Fig. S2 Nitrogen adsorption/desorption isotherms of (a) Pd/GN2 and (b) Pd/GN1. (The surface areas of Pd/GN2 and Pd/GN1 are 182.56 m$^2$/g and 162.56 m$^2$/g respectively).

Fig. S3 TGA curves of Pd/GN2 and Pd/GN1 catalysts.

As shown in Fig. S3, two catalysts appear three significant drops in mass. The appearance of the first mass drop around 160 °C is attributed to the evolution of CO$_2$ and CO from the remnant oxygenated groups on graphene surface. The second drop in mass around 400 °C is assigned to the combustion of graphene carriers. In proceeding heating, the Pd NPs in catalysts were easily oxidized to palladium oxide. So the third drop in mass appears around 825 °C due to the decomposition of palladium oxide at high temperature. The final residua are pure palladium, which content is 32% in weight.
**Fig. S4** TEM of Pd/GN2 with different Pd loading content on graphene: (a) 18 wt%, (b) 25 wt%, (c) 40 wt%, (d) 50 wt%. (e) Average particle size-Pd content dependence of Pd/GN2 catalysts with different Pd loading content (TEM of Pd/GN2 with 32 wt% Pd loading content and particle size of Pd on graphene are shown in Fig.1c and Fig. S1c).

**Fig. S5** Cyclic voltammograms of formic acid electro-oxidation on the Pd/GN2 with different Pd loading content: (a) 18 wt%, (b) 25 wt%, (c) 40 wt%, (d) 50 wt%, ( inset is the current density-time dependence of formic acid electro-oxidation on the corresponding Pd/GN2 catalysts). (e) Current density-Pd content dependence of formic acid oxidation (□—□) and the residual current of formic acid electro-oxidation on the different Pd/GN2 catalyst electrodes after 3600s (●—●). (Cyclic voltammogram of formic acid electrooxidation on Pd/GN2 with 32 wt% Pd loading and the residual current of formic acid eletrooxidation after 3600s are shown in Fig.6b and 6c.)
respectively).