Supporting Information

Synthesis and Assembly of Pd Nanoparticles on Graphene for Enhanced Electrooxidation of Formic Acid

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Materials and Methods

Materials. Oleylamine (OAm, >70%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%) and borane-morpholine (MB, 95%) were purchased from Sigma-Aldrich. Palladium acetlyacetonate ($Pd(acac)_2$, 99%) were purchased from Strem. The deionized water was obtained from a Millipore Autopure system. All the reagents were of analytical grade and used without further purification.

Characterization. Transmission electron microscopy (TEM) was performed on a Philips CM 20 with an accelerating voltage of 200 kV. All the TEM samples were prepared by depositing a drop of diluted nanparticles (NPs) dispersion in hexane on copper grid coated with carbon film. X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8-Advanced diffractometer with Cu Kα radiation (λ=1.5418 Å). Electrochemical measurements were carried out by a Pine Electrochemcial Analyzer, model AFCBP1 with Ag/AgCl (4 M KCl) and Pt wire as reference and counter electrodes, respectively.

Synthesis of 4.5 nm Pd Nanoparticles. 0.1 g $Pd(acac)_2$ (0.328 mmol) was added into ODE (8 mL) and OAm (10 mL), and the mixture was heated to 100 ºC under N_2 protection to form a solution. 0.2 g MB

dissolved in 2 ml OAm was injected into the above solution. The solution was then heated to 130 ºC at the heating rate of 4-5 ºC/min and kept at this temperature for 20 min. The Pd nanoparticles were separated by adding ethanol (20 mL) and centrifugation. The particles were washed with ethanol twice and then dispersed in hexane.

Synthesis of Graphene. 100 mL of dimethylformamide (DMF) dispersion of GO (1 mg/mL) and 4 mL ammonium hydroxide (25% wt.) was heated to refluxing and kept at this temperature for 6 h to convert graphene oxide (GO) to graphene (G).[1] The solution was cooled down to room temperature.

The Preparation of C-Pd NPs and G-Pd NPs. (a) C-Pd NPs: 20 mg of the as-synthesized Pd NPs and 20 mg of Ketjen carbon support were mixed in 40 mL hexane and sonicated with a Fischer Scientific FS 110 for 60 min. The product was then centrifugated (8500 rpm 8min). The power producttt was collected and washed with ethanol three times before they were dried under N_2. **(b) G-Pd NPs:** 20 mg of Pd NPs dispersed in 20 mL of hexane was added into 20 mL of DMF solution of G (1 mg/mL) and the mixture was sonicated for 1 h. The product was then centrifugated (8500 rpm 8 min), and was washed with ethanol two times before they were dried under N_2.

Electrochemical Measurements. The C-Pd NP and G-Pd NP catalysts were cleaned with acetic acid as reported.[2] Then, they were further dispersed in deionized water + isopropanol + 5% Nafion (volume ratio: 4/1/0.025) to reach a concentration of 2 mg/mL. After sonicating for 1 h, 20 µL of the catalyst was dropped on a glassy carbon (GC) electrode and dried overnight under ambient conditions. Cyclic votalmmgramms (CVs) was conducted in a 0.1 M $HClO_4$ solution in the presence of N_2 at a scan rate of 50 mV/s. Electro-catalysis was carried out in a 0.1 M $HClO_4$ +0.1 M HCOOH solution at a scan rate of 50 mV/s.

References

1. S. Guo and S. Sun, *J. Am. Chem.Soc.* 2012, **134**, 2492-2495.
2. V. Mazumder and S. Sun, *J. Am. Chem. Soc.* 2009, **131**, 4588-4589.

Figures

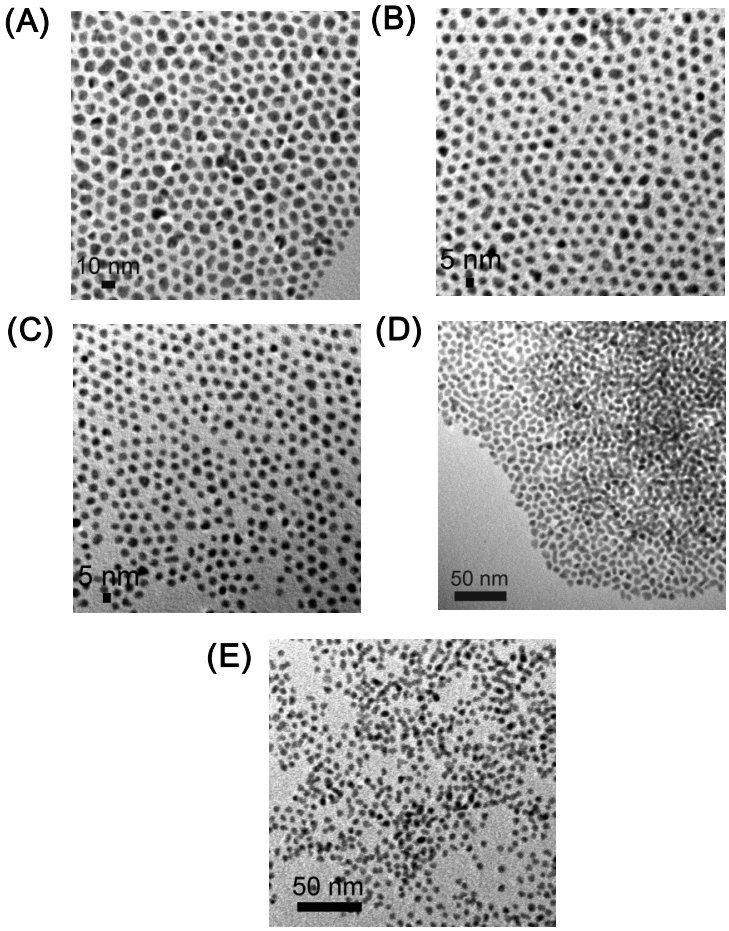

Figure S1. TEM images of Pd NPs prepared in different synthetic conditions: (A) 10 mL OAm, 8 ml ODE, 0.2 mg MB, 80 ^{o}C injection; (B) 4 mL OAm, 14 mL ODE, 0.2 mg MB, 100 ^{o}C injection; (C) 1 mL OAm, 17 mL ODE, 0.2 mg MB, 100 ^{o}C injection; (D) 6 ml OAm, 4 mL OA, 8 mL ODE, 0.2 mg MB, 100 ^{o}C injection; (E) 3 mL OAm, 7 mL OA, 8 mL ODE, 0.2 mg MB, 100 ^{o}C injection.