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Supporting Information

Amine-borane assisted synthesis of wavy palladium nanorods on graphene as efficient catalyst for formic acid oxidation

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Experimental section:

Chemicals and materials. Potassium permanganate ($KMnO_4$, Shanghai Chemic Co., Ltd, ≥99.5%). Ethanol (C_2H_5OH, >99.8%), hydrogen peroxide (H_2O_2, ≥30%), sulfuric acid (H_2SO_4, 95~98%), phosphoric acid (H_3PO_4, ≥85%), N, N-dimethylformamide (C_3H_7NO, ≥99.5%), graphite power (EC 300J, ≥99.85%) were purchased from Sinopharm Chemical Reagent Co., Ltd., *N, N*-diethylaniline borane ($C_{18}H_{15}N \cdot BH_3$, >98%), 2-metylpyridine-borane complex ($C_6H_{10}BN$, >85%), triethylamine-borane ($C_6H_{18}BN$, >90%) were purchased from TCI Shanghai Co., Ltd. Palladium acetylacetonate ($Pd(acac)_2$, >98%)， palladium chloride($PdCl_2$, >99%), palladium acetate ($Pd(OAc)_2$, >98%) were purchased from Wuhan Greatwall Chemical Co., Ltd. Oleylamine (80~90%) was purchased from Aladdin Industrial Corporation. All chemicals were used as obtained. We use ordinary distilled water as the reaction solvent.

Synthesis of graphite oxide. Here we use an improved method[1], a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was added to graphite flakes (3.0 g, 1 wt equiv). Under continuous stirring, $KMnO_4$ (18.0 g, 6 wt equiv) was added partially to prevent the temperature of the reaction from increasing too high. The reaction was then heated to 50 °C and stirred for 12 h. The reaction was cooled to room temperature and poured into the mixture of deionized water (400 mL) and 30% H_2O_2 (3 mL) which was placed into the ice-bath. The resultant solution was centrifuged to obtain the product. Centrifuged product was then washed in succession with 200 mL of water, 200 mL of 30% HCl, 200 mL of ethanol and dried under vacuum at 25 °C.

Synthesis of graphene. Graphene was prepared by the method reported in the literature[2]. 250 mg graphite oxide was dispersed in 500 mL *N, N*-dimethylformamide, then the mixture was heated to refluxing for 6 h. After cooling down to the room temperature, the solid precipitate was collected by vacuum filtration. The product was washed by water and ethanol and dried under vacuum at 50 °C.

Synthesis of Pd nanocrystals. Under a nitrogen flow, 0.1mmol $Pd(acac)_2$ was mixed with 10 mL oleylamine (OAm). The formed solution was heated to 60 °C, resulting in a near colorless solution.

And the mixture kept at this temperature for 1 h to remove oxygen. 100 μL *N, N*-diethylaniline-borane was quickly injected into the Pd-OAm solution. A visible color change from colorless to a brown-black was observed. The temperature was raised to 90 °C and kept at this temperature for 60 min. Next the solution was cooled down to room temperature. Ethanol was added to precipitate the NPs, and the product was collected by centrifugation at 8500 rpm for 10 min. The obtained nanocrystallites were further washed twice in ethanol and dried by oil pump vacuum at 50 ^{o}C for 3 h to give Pd Nanorods as a dark gray powder. Other types of Pd nanocrystallites were also prepared using the same procedure except for the use of different precursors or different reducing agents, which are described in detail in the results and discussion section.

Synthesis of Pd/graphene (20% loading) from Pd Nanorods. 8 mg of Pd NPs were dissolved in 10 mL hexane in a 25 mL vial and 32 mg of graphene support was carefully added to it. This colloidal mixture was sonicated for 10 min, and then stirred 12 h (to ensure complete adherence of Pd Nanorods onto the graphene support) under a nitrogen flow. After evaporation of hexane, 15 mL of acetic acid was added to the Pd/graphene dispersion and heated for 10 h at 70 °C. The reaction mixture was cooled down to room temperature. 30 mL of ethanol was added and the mixture was centrifuged at 8500 rpm for 8 min. This procedure was repeated twice. The resultant Pd/graphene Nanorods were weighed. A measured amount of deionized water was added, resulting in a 5 mg/mL solution. This mixture was sonicated for 1 h to ensure uniform distribution. All catalytic studies were carried out using 2 μL of this catalyst. For comparison, Pd/XC-72 and Pd/EC 300J were also prepared by a similar method, while graphene was replaced by Vulcan XC-72 or EC 300J.

Physical Characterization. TEM images were obtained using a FEI Tecnai G20 U-Twin TEM instrument operating at 200 kV. Powder X-ray diffraction (XRD) patterns were measured by a Bruker D8-Advance X-ray diffractometer using Cu Ka radiation source (λ=0.154178 nm) with a velocity of 6^{o} min^{-1}. X-ray photoelectron spectroscopy (XPS) measurement was performed with a Kratos XSAM 800 spectrophotometer. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on IRIS Intrepid II XSP (Thermo Fisher Scientific, USA). The electrochemical measurements were performed on CHI660A electrochemical workstation (ShanghaiChenhua Co., China)

Electrochemical Measurements. Electrochemical measurements were performed using a three-electrode cell at room temperature. A Glassy Carbon Electrode (GCE) (5 mm diameter) was used as the substrate of the working electrode. A standard calomel electrode(SCE) was used as the reference electrode, which was separated from the working electrode by a Luggin capillary to prevent chloride ions from cross-contaminating the electrolyte in the working cell, and a Pt sheet was used as the counter electrode. To prepare the working electrodes, 2.5 mg of the 20 wt% graphene-supported catalysts were dispersed into 1mL 0.1% Nafion solution. After ca. 30 minutes' sonication, 2 μL of the dispersion was transferred onto the GCE with a micropipette and then let to dry in air. Before transferring into the working solution (0.1 M $HClO_4$), the prepared thin-film electrodes was first immersed into 75 ℃ 0.1M $HClO_4$ solution for 10 seconds to improve the wetting ability of the film with the solution.

To record the CO striping voltammetric responses, the solution was first purged with CO gas for ca. 30 min. while keeping the electrode potential constantly at -0.18 V; Ar gas was then bubbled into solution for ca. 30 min. under the same potential to remove the CO in the solution. The CO stripping curve is then recorded by sweeping potentialfrom -0.18V to 0.85 V with a potential sweeping rate of 20 mV/s.

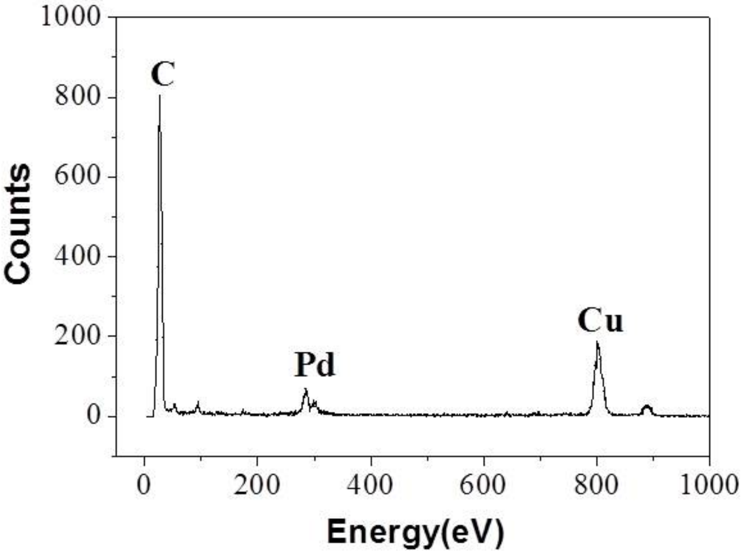

Fig. S1. EDX image of the the Pd Nanorods.

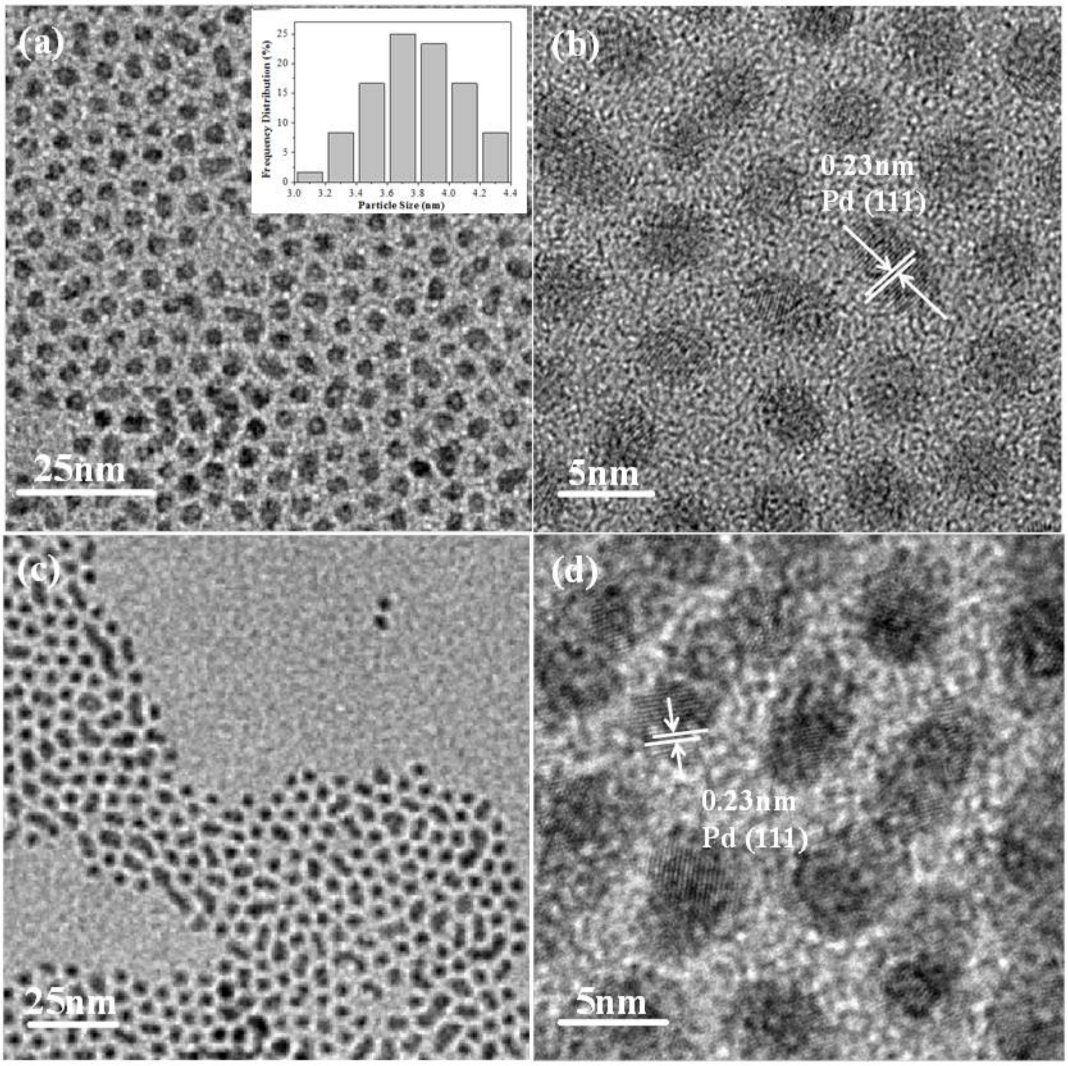

Fig. S2. TEM images of Pd nanostructures prepared using the standard procedure, except for the change of reducing agent: a) - b) triethylamine-borane, c) - d) 2-metylpyridine-borane. The inner figures are the particle distribution.

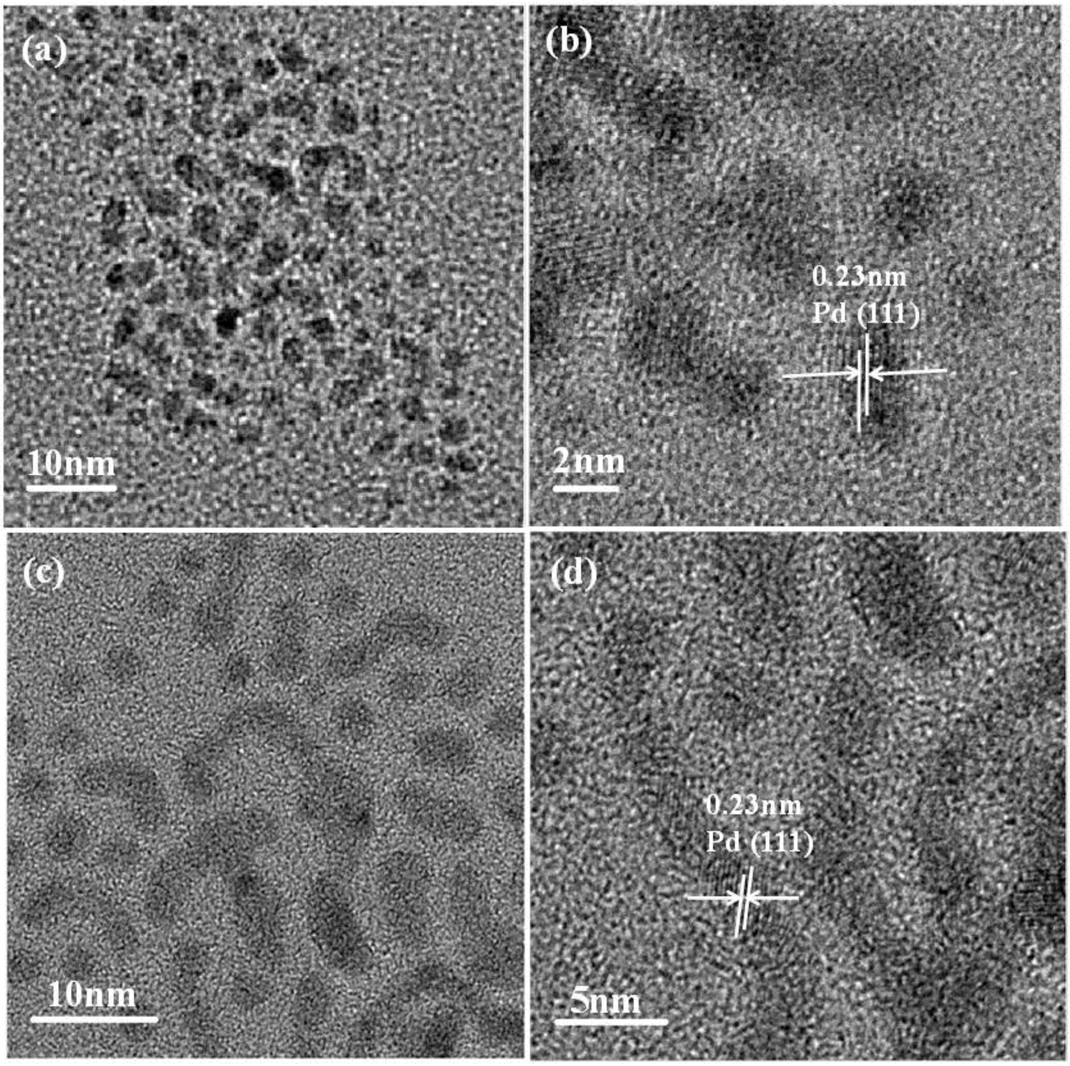

Fig. S3. TEM images of Pd nanocrystallites prepared with different Pd precursors. a) - b) $PdCl_2$ and c) - d) $Pd(OAc)_2$.

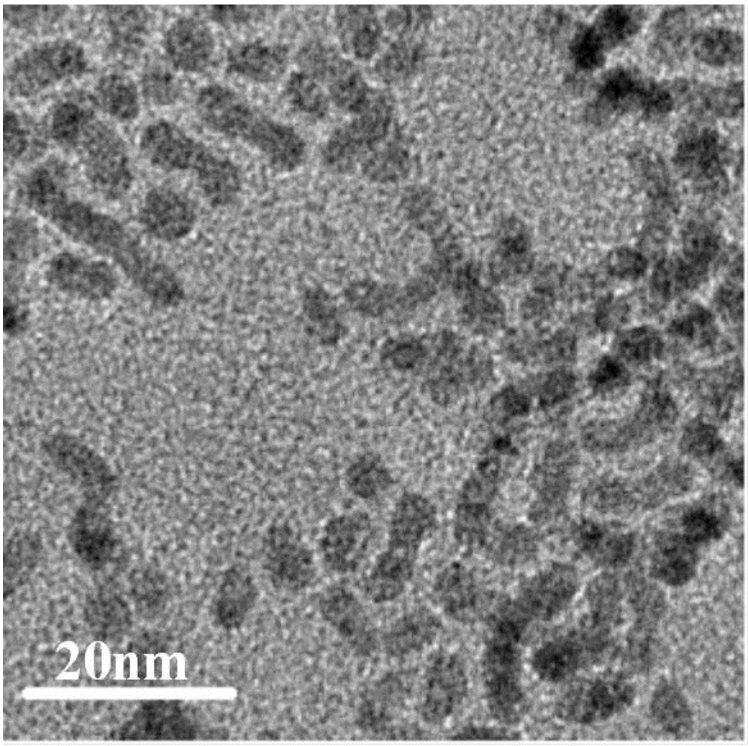

Fig. S4. TEM image of the Pd nanorods supported on graphene. Pd nanorods were reduced by *N, N*-diethylaniline-borane.

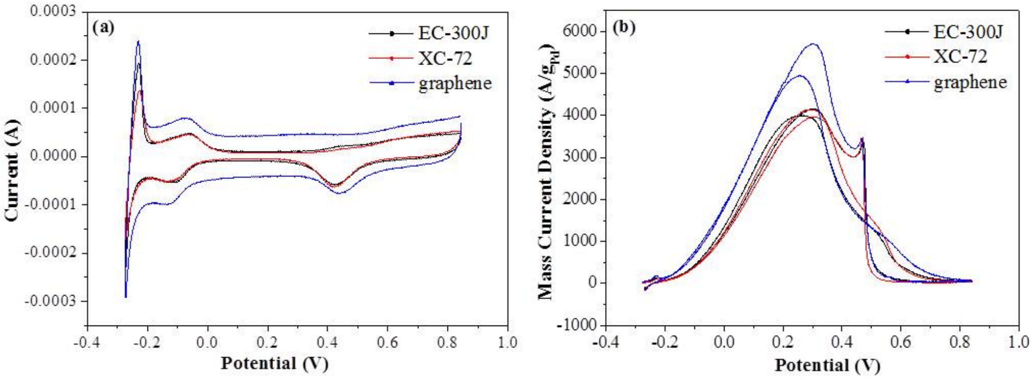

Fig. S5. a) CVs of the Pd NRs with three different supports at 25 °C in N_2 saturated 0.1 M $HClO_4$ (scan rate: 50 mV/s). b) NP mass current densities vs applied potential in 0.1 M $HClO_4$ and 2 M HCOOH at 25 °C (scan rate: 10 mV/s).

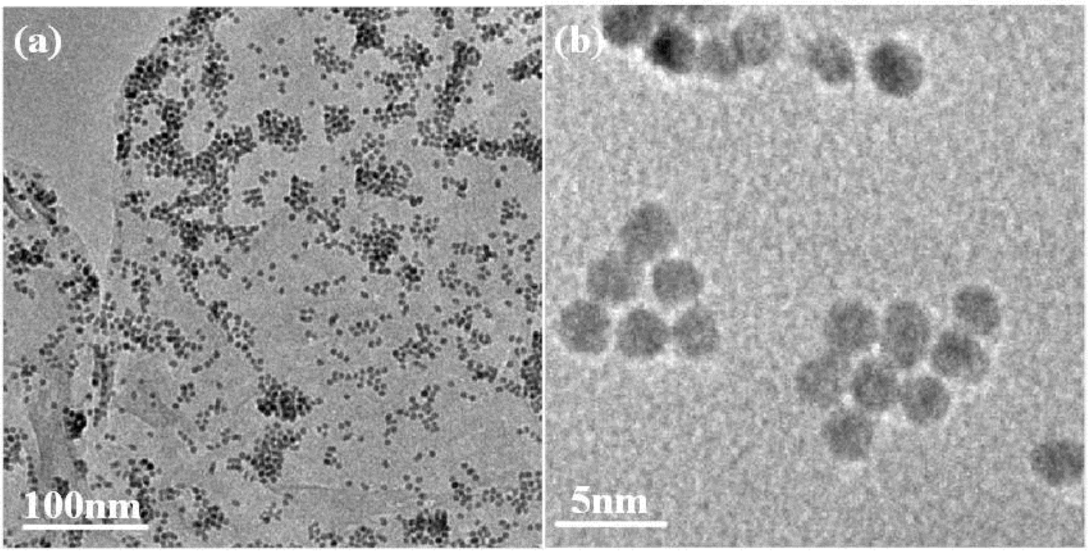

Fig. S6. TEM image of the Pd nanoparticles supported on graphene. Pd nanoparticles were reduced by triethylamine-borane.

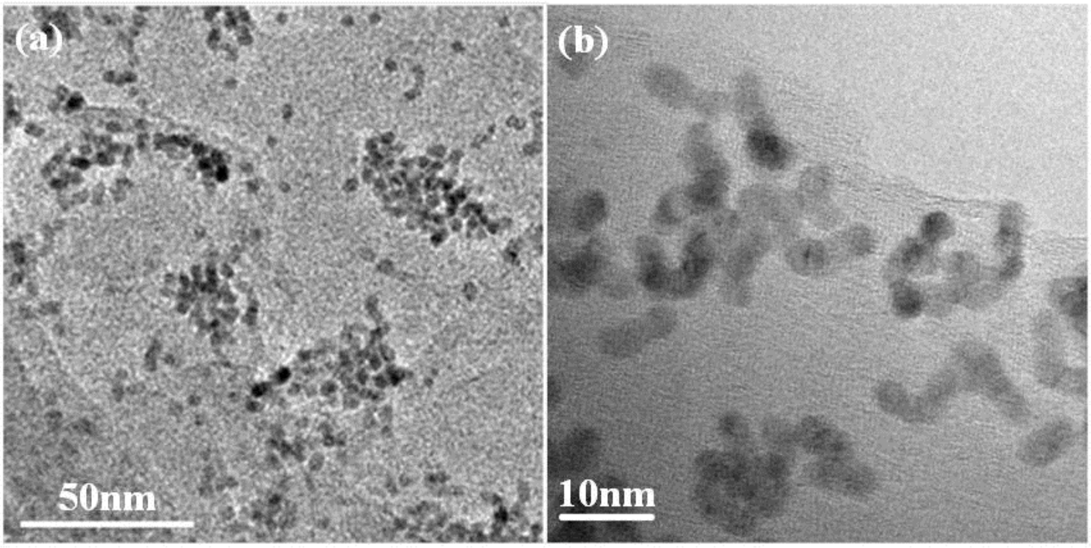

Fig. S7. TEM image of the Pd nanocrystallites supported on graphene. Pd nanocrystallites were reduced by 2-metylpyridine-borane complex.

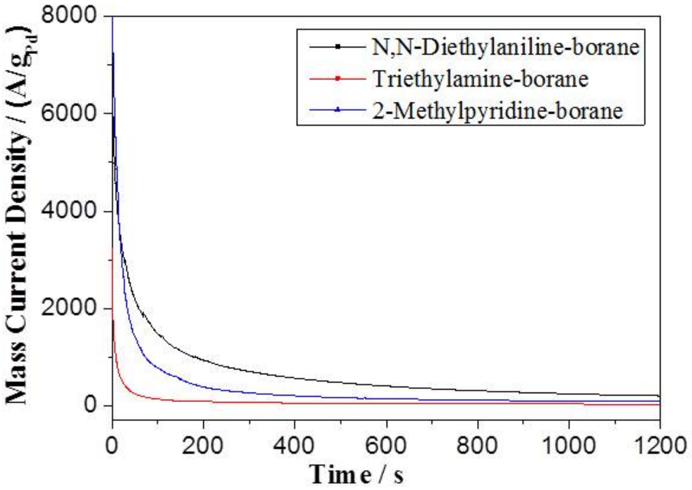

Fig. S8. Chronoamperometric curves of graphene-supported Pd nanocrystallites prepared by different reducing agents. The curves were recorded in 2 M HCOOH + 0.1 M $HClO_4$ aqueous solutions at 0.3 V (vs. SCE).

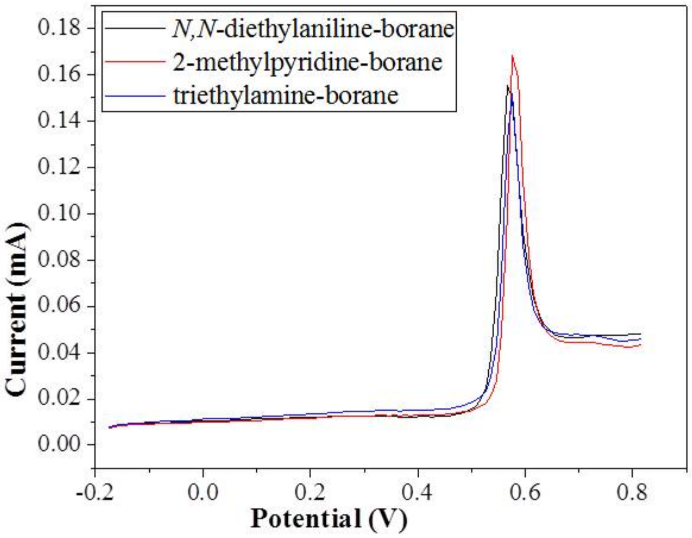

Fig. S9. CO stripping curves of graphene-supported Pd nanocrystallites prepared by different reducing agents in 0.1 M $HClO_4$ solution.

References:

1 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano* 2010, **4**, 4806.

2 S. J. Guo and S. H. Sun, *J. Am. Chem. Soc.* 2012, **134**, 2492.