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Supporting Information

Pristine graphene dispersion in solvents and its application as a catalyst support: a combined theoretical and experimental study

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Theoretical calculations

The density functional theory (DFT) calculations were performed using the Gaussian 09 program[1] at the B3LYP/6-311+G(d,p) level, where the D3 dispersion correction was used to better describe the weak interaction between graphene and solvent molecules[2] and the PCM mode was applied to include the solvent effect.[3] The interaction between graphene and solvent molecule is evaluated by the adsorption energy (E_a) as

$$E_a = E_{m-graphene} - E_m - E_{graphene}$$

where E_m, $E_{graphene}$, *and* $E_{m\text{-}graphene}$ are the energy of an isolated solvent molecule, graphene, and molecule-graphene system respectively. The basis set superposition error (BSSE) was applied to correct the adsorption energy.[4]

The D3 correction developed by Grimme et al has been proved to give reasonable and accurate description for the weak interaction between molecules.[2] The dispersion energy could be calculated as

$$E^{DFT-D3}_{disp} = -\frac{1}{2}\sum_{A \neq B}\sum_{n=6,8} s_n \frac{C^{AB}_n}{R^n_{AB}} f_{damp,n}(R_{AB})$$

where R_{AB} is the internuclear distance of an atom pair AB, C_n^{AB} is the averaged nth-order dispersion coefficient, s_n is the global scaling factor, $f_{damp,n}$ denotes the damping function used to determine the range of dispersion correction which is described as

$$f_{damp,n}(R_{AB}) = -\frac{1}{1 + e^{-\gamma\left(R_{AB}/s_{r,n}R^{AB}_0 - 1\right)}}$$

where R_0^{AB} is a cut-off radius for atom pair AB.

The plots of the electron density (ρ) and reduced density gradient were generated using Multiwfn program.[5]

Synthesis of Pd/G

10 mg $PdCl_2$ was added in 3 mL THF, and moderate concentrated HCl was added to the solution with stirring until $PdCl_2$ was dissolved completely. 24 mg single layer graphene (Xianfeng Nano, China) was added in the above solution, and catalyst slurry could be obtained after continuous stirring and sonication. The catalyst slurry was dried at 40°C in oven, and ground to a fine powder in an agate mortar. The Pd catalyst (20 wt.%) supported on graphene was thereafter reduced with H_2 at 120°C for 2 h with the protection of N_2.

Characterization

The dispersion and deposition of Pd/G catalysts were examined using a JEOL JEM-2100F transmission electron microscope (TEM) operated at 200 kV and histograms of the catalysts were obtained by examining more than 200 particles on the TEM micrographs. Powder X-ray diffraction (XRD) patterns for the samples were obtained on a Rigaku D/Max 2500V/PC X-ray diffractometer using Cu Kα radiation source operating at 40 kV and 30 mA. The XRD profile was recorded at a scan rate of 4°/min for 2θ values between 15° and 85°. The XPS analysis was carried out using ESCALAB 250Xi spectrometer with an Al Kα radiator.

Electrochemical measurements

Electrochemical measurements were carried out using CHI660C electrochemical workstation. A conventional, three-electrode cell consisting of a glass carbon (GC) electrode with a diameter 5 mm as the working electrode, Pt wire as the counter electrode and a reversible hydrogen electrode (RHE) in the same electrolyte as the reference electrode[6] was used for the electrochemical measurements. All potentials throughout this paper were referred to RHE. 3 mg catalyst powder was dispersed ultrasonically in 0.5 mL diluted Nafion alcohol solution (0.05 wt.%) to form an ink. 10 μL of the ink was pipetted onto a GC electrode surface and dried at infrared lamp. After solvent evaporation, a thin layer of Nafion-bonded catalyst was deposited on the GC surface to serve as the working electrode. Liner circle voltammetry (LCV) was carried out at room temperature in a deaerated 1.0 M formic acid + 0.5 M H_2SO_4 solution at a scan rate of 10 mV s^{-1} to evaluate the catalyst activity for the formic acid oxidation reaction. Chronoamperometry (CA) test was conducted in a nitrogen saturated 1.0 M formic acid + 0.5 M H_2SO_4 solution at 0.4 V (vs. RHE). For CO stripping voltammetry, CO was adsorbed at 0.0 V (RHE) in 0.5 M H_2SO_4 solution for 30 min, excess CO in the electrolyte was then purged out with N_2 for 60 min.

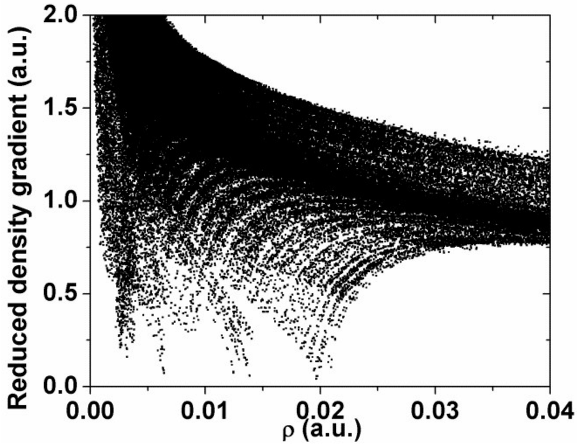

Fig. S1 Plot of the electron density (ρ) and reduced density gradient for acetone molecule adsorbed on graphene. The plot is similar with that of THF, indicating there is also van der Waals interaction between acetone molecule and graphene.

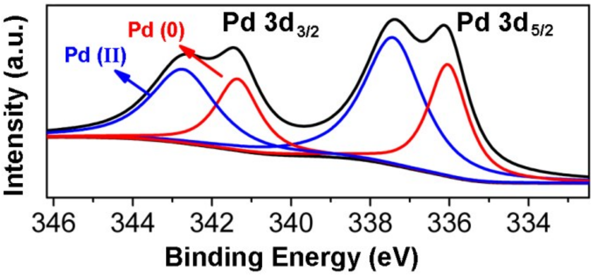

Fig. S2 Pd 3d XPS spectrum of Pd nanoparticles supported on graphene.

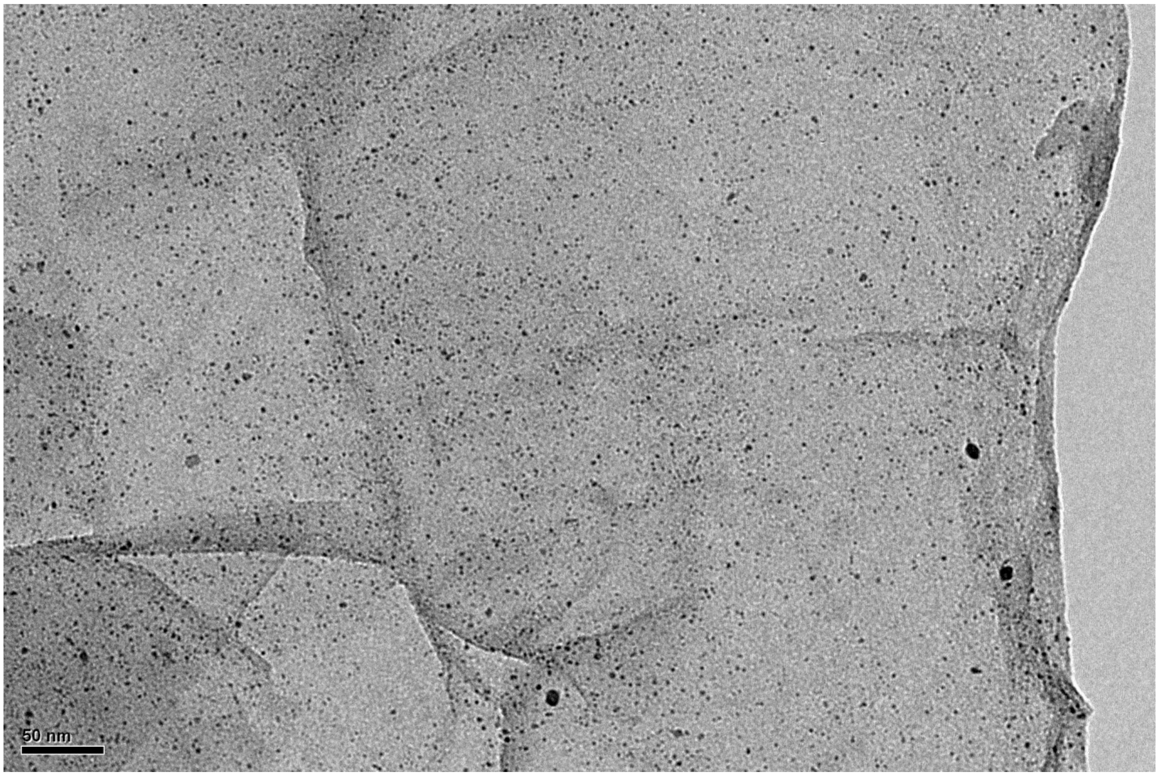

Fig. S3 TEM image of Pd particles (20 wt.%) on graphene using THF as solvent in the synthesis process. Pd particles are well dispersed on graphene.

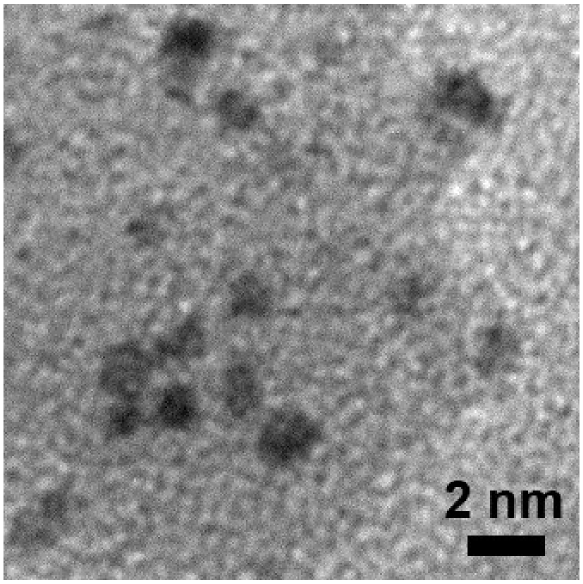

Fig. S4 High-resolution TEM image of Pd/G.

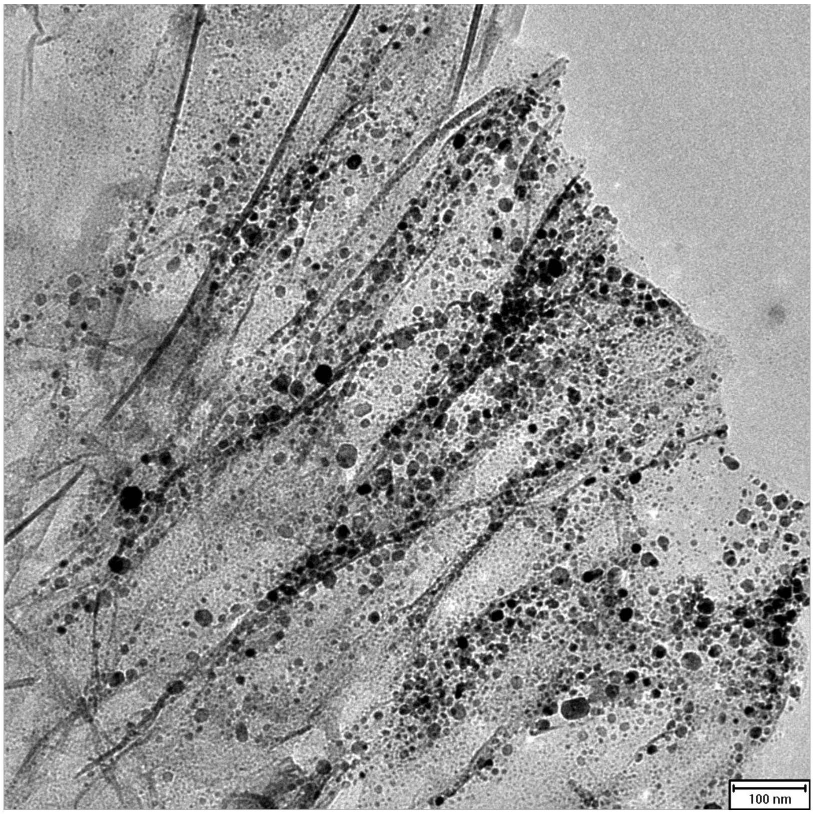

Fig. S5 TEM image of Pd particles (20 wt.%) on graphene using water as solvent in the synthesis process. Pd particles are agglomerated with much larger size than those synthesized using THF solvent.

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