Electronic Supplementary Material (ESI) for Green Chemistry

Integrated Electrocatalytic Processing of Levulinic Acid and Formic Acid to Biofuel Intermediate Valeric Acid

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Support Information

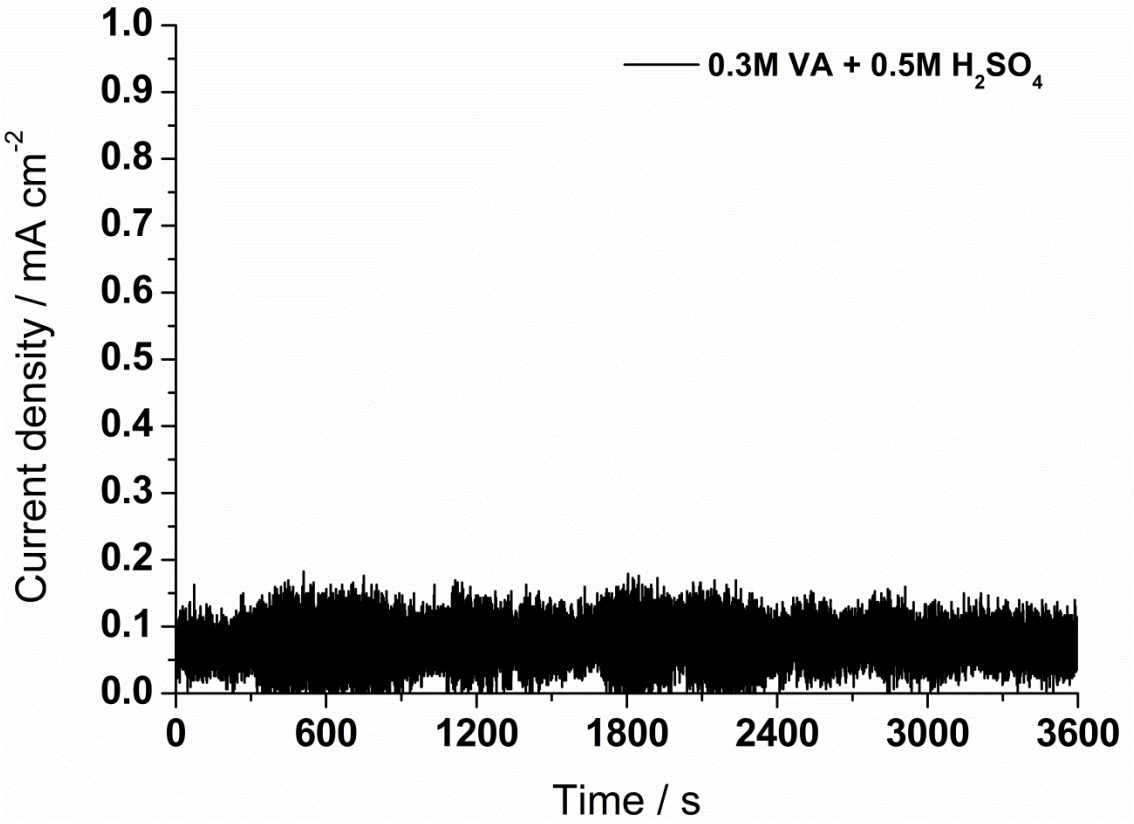
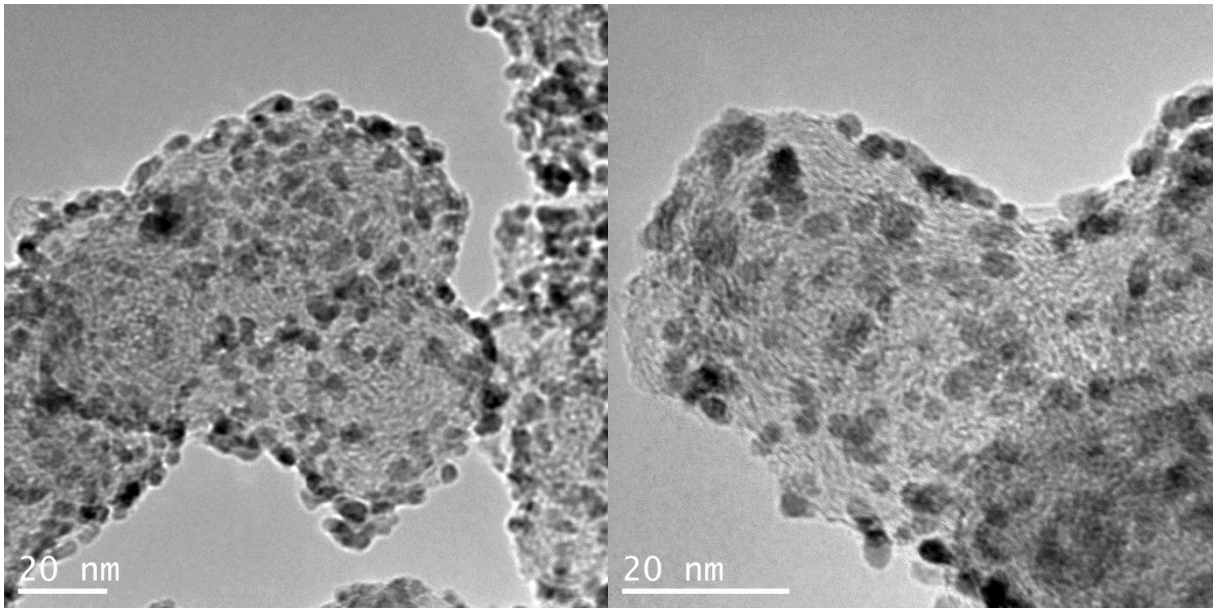


Fig S1 Current density as a function of time for electro-oxidation of valeric acid. Reaction conditions: constant fuel-cell voltage of 0.1V, anode: 0.3 M VA + 0.5 M H_2SO_4 with 1 ml min^{-1} fed over 3.0mg cm^{-2} Pd/C-40wt%, cathode: oxygen of 400 ml min^{-1} fed over 3.0mg cm^{-2} Pt/C-40wt%.



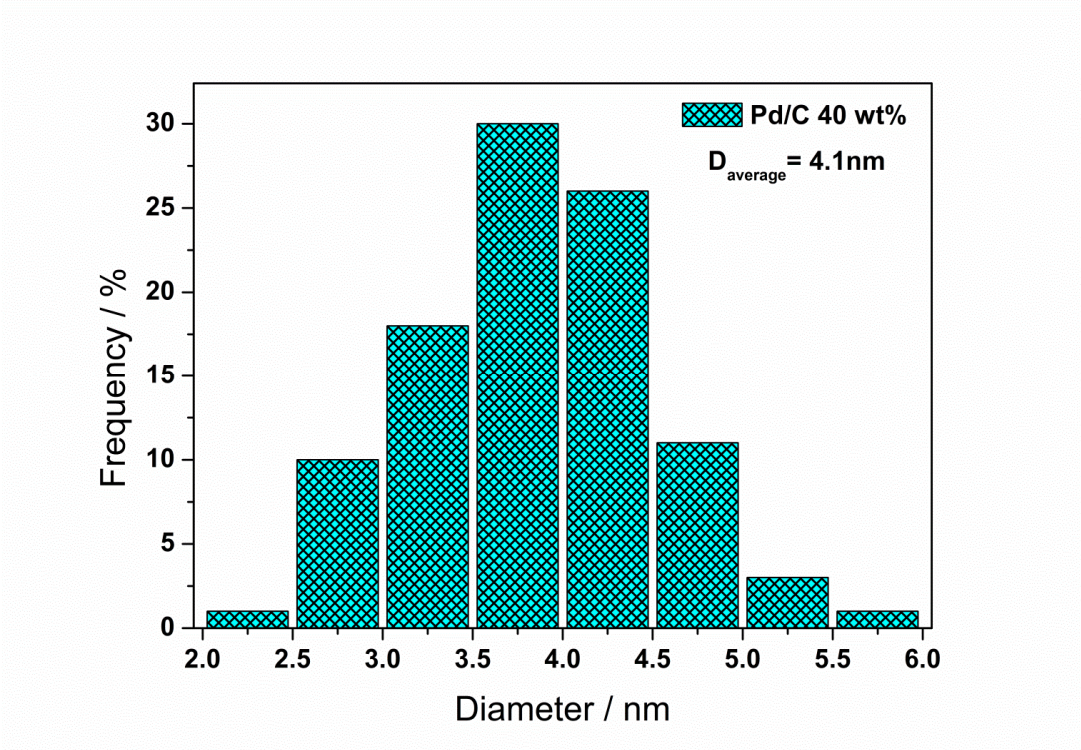
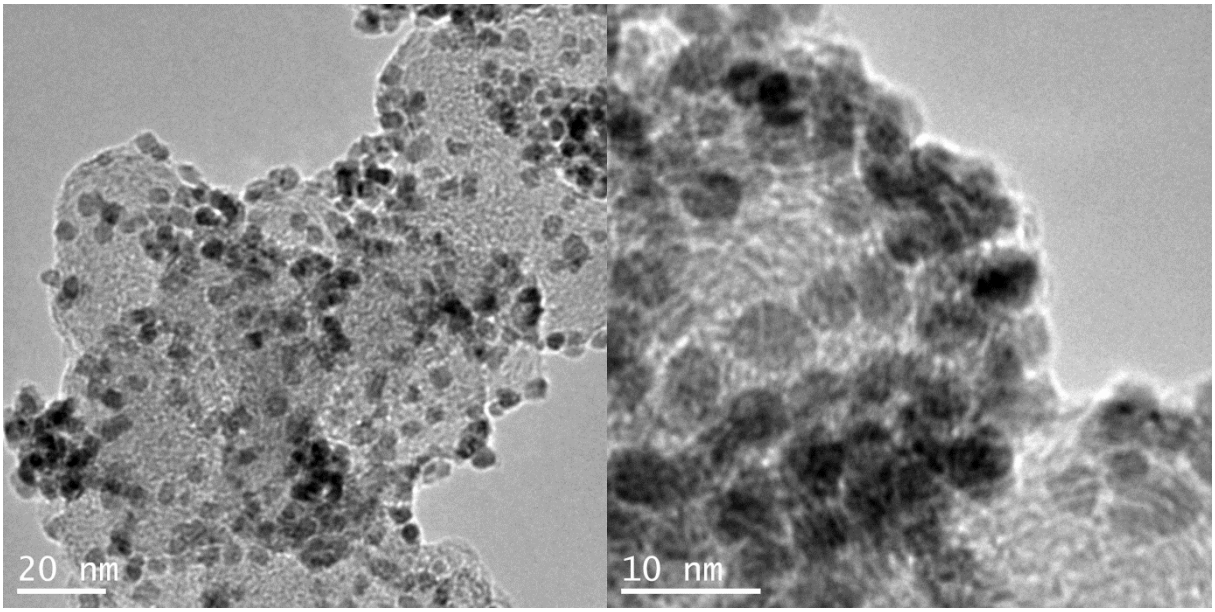


Fig.S2 TEM images and corresponding particle-size histograms of synthesized Pd/C catalyst after 6 hours formic acid electro-oxidation



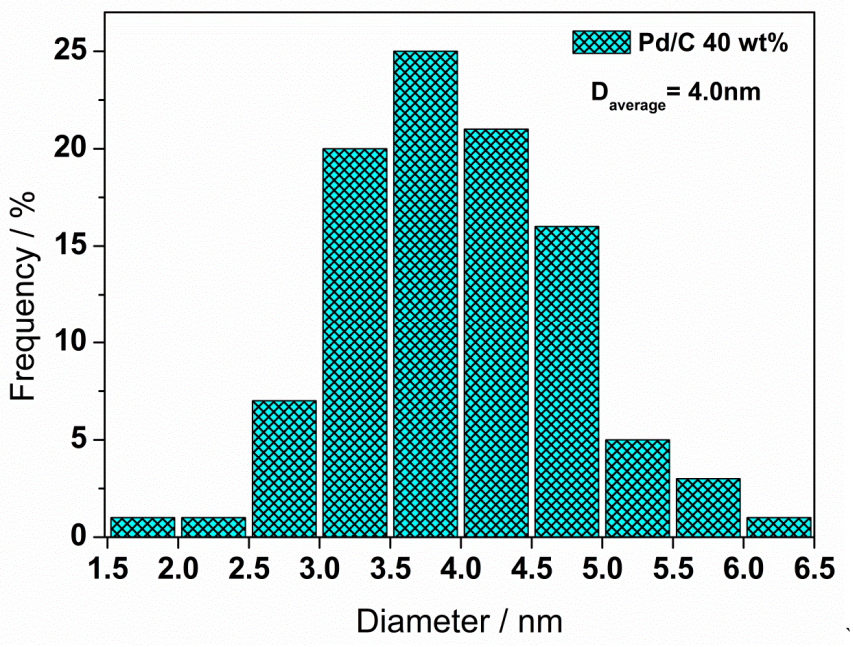


Fig. S3 TEM images and corresponding particle-size histograms of synthesized Pd/C catalyst before 6 hours formic acid electro-oxidation.

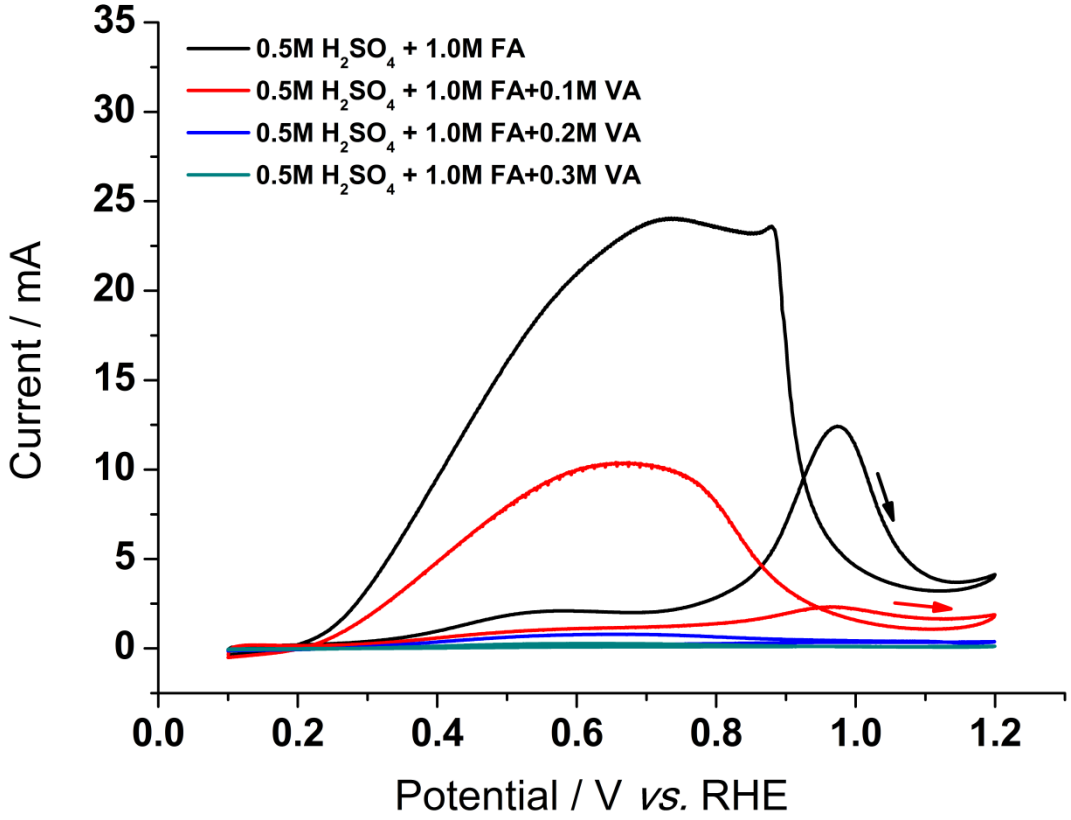


Fig.S4 Cyclic voltammograms of Pt/C-40wt% catalyst with valeric acid concentrations of 0, 0.1, 0.2 and 0.3M in 1.0M formic acid + 0.5M H_2SO_4 solution, at 50mV s^{-1}, room temperature.

The VA effect on the electro-catalytic oxidation of FA on Pt/C catalyst was investigated by the cyclic voltammograms of Pt/C-40wt%, in 0M, 0.1M, 0.2M and 0.3M VA +1.0M FA + 0.5M H_2SO_4 solution. Similar to Pd/C-40wt% catalyst, the peak currents for FA electro-oxidation on Pt/C-40wt% catalyst are decreased to 2.32 mA, 0.34 mA and 0.11 mA, with the VA concentration increasing to 0.1 M, 0.2M and 0.3M, respectively, as shown in Fig. S2.

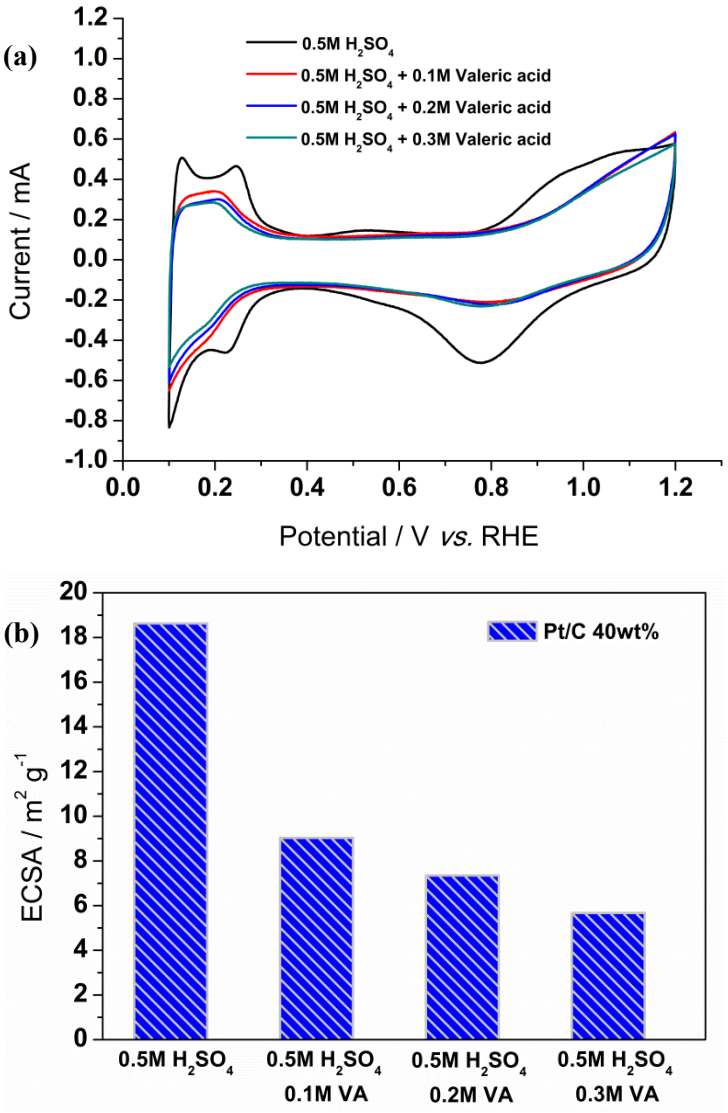


Fig.S5 (a) Cyclic voltammograms and (b) ECSA of Pt/C-40wt% catalyst with VA concentrations of 0M, 0.1M, 0.2M and 0.3M + 0.5M H_2SO_4 solution, at 50mV s^{-1}, room temperature.

The cyclic voltammetograms of Pt/C-40wt% in 0M, 0.1M, 0.2M and 0.3M VA + 0.5M H_2SO_4 aqueous solution are shown in Fig. S3. The ECSA of Pt/C-40wt% calculated based on the hydrogen desorption peak are decreased from 18 m^2/g (0 M VA) to 9.0 m^2 g^{-1}, 7.3 m^2 g^{-1} and 5.7 m^2 g^{-1}, with the VA concentration increasing to 0.1M, 0.2M and 0.3M, respectively, indicating a higher VA concentration leads to a greater ECSA loss.

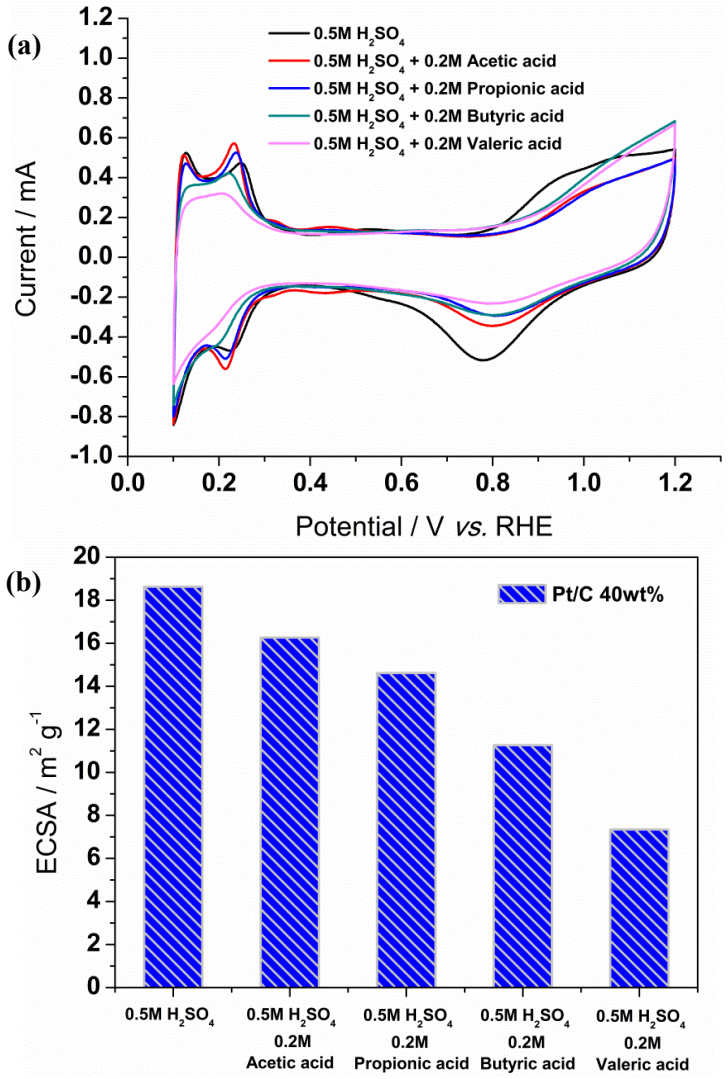


Fig.S6 (a) Cyclic voltammograms and (b) ECSA of Pt/C-40wt% catalyst with 0.2 M acetic acid, propionic acid, butyric acid or valeric acid in 0.5 M H_2SO_4 solution, at 50mV s^{-1}, room temperature.

Fig. S4 shows cyclic voltammetograms of Pt/C-40wt% in 0.2M carboxylic acid (acetic acid, propionic acid, butyric acid and valeric acid)) + 0.5 M H_2SO_4 solution. With the carbon chain length increasing (from C_2 to C_5), the ECSA of Pt/C calculated from the hydrogen desorption peak deceased to 16.3 m^2 g^{-1} (with acetic acid), 14.6 m^2 g^{-1} (with propionic acid), 11.3 m^2 g^{-1} (with butyric acid), and 7.3 m^2 g^{-1} (with valeric acid), indicating that carboxylic acids of longer carbon chains lead to a greater ECSA loss.

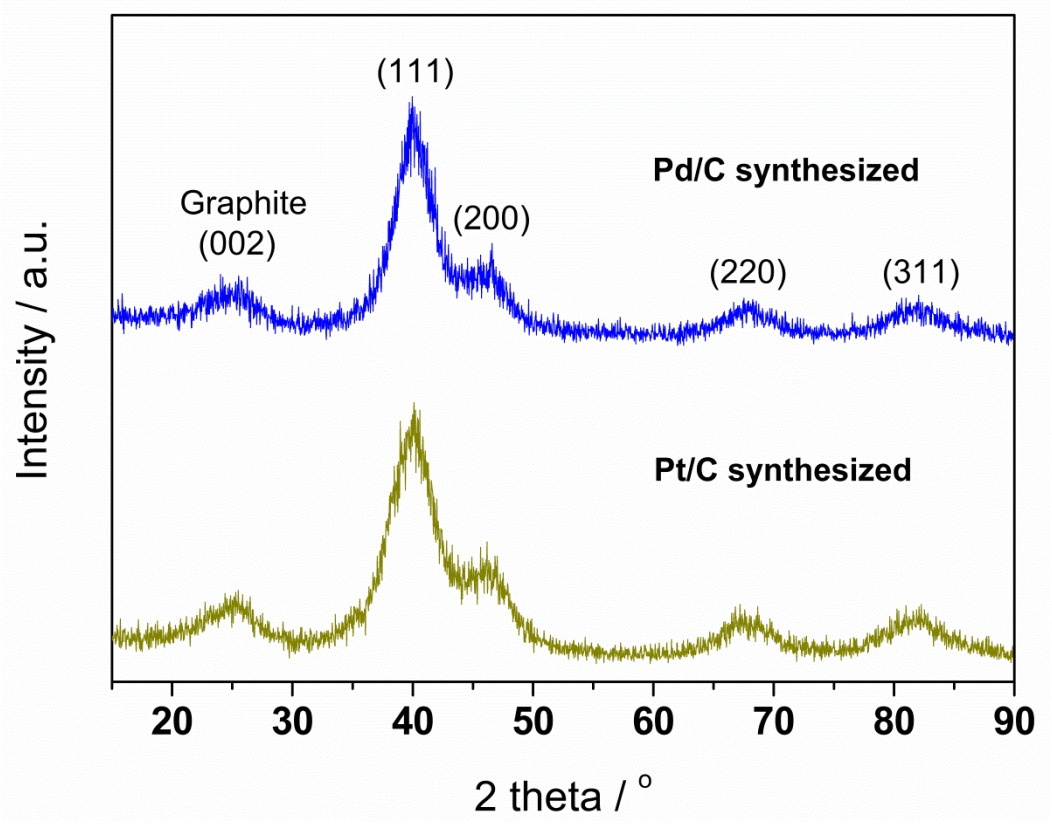


Fig.S7 XRD patterns of synthesized Pd/C and commercial Pd catalysts.

The average crystal grain size of Pt/C and Pd/C can be estimated based on the Debye–Scherrer equation:

$$L = \frac{0.9\lambda_{K_\alpha}}{B_{2\alpha} \times \cos\theta_{\max}} \qquad \text{Eq. S1}$$

where L is the mean crystal size, λ is the wavelength of the X-ray (1.5406 Å), $B_{2\beta}$ is the full width at half-maximum of the peak (rad), and θ_{max} is the Bragg angle (rad). From the calculation based on (220) diffraction peak, the particle sizes of Pt/C and Pd/C are 3.8 nm and 3.4 nm, respectively.