

Supporting Information

Pd₃Co₁ Alloy Nanocluster on the MWCNT Catalyst for Efficient Formic Acid Electro-Oxidation

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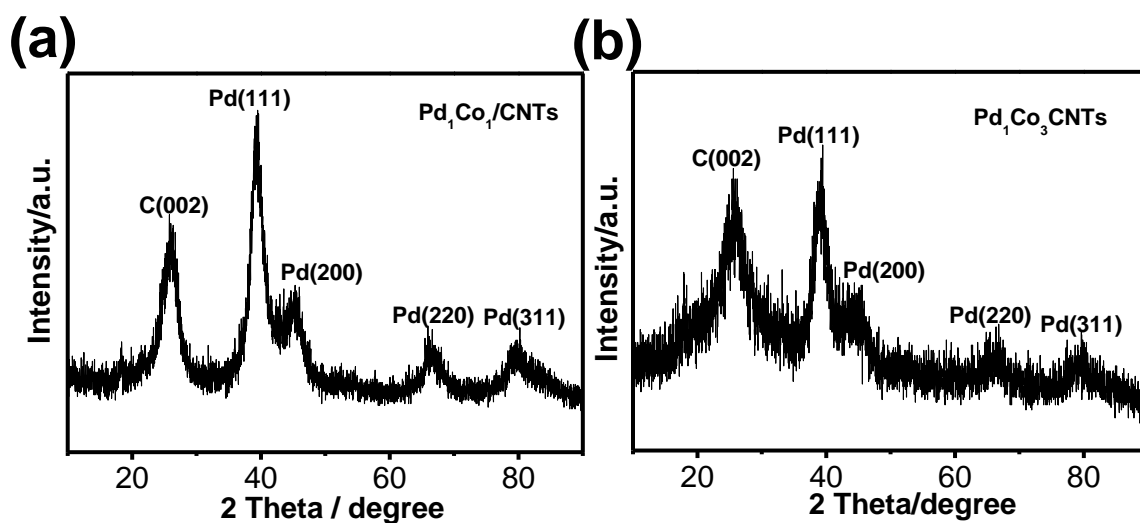


Figure S1. XRD patterns of Pd₁Co₁/CNTs (a) and Pd₁Co₃/CNTs (b) catalysts.

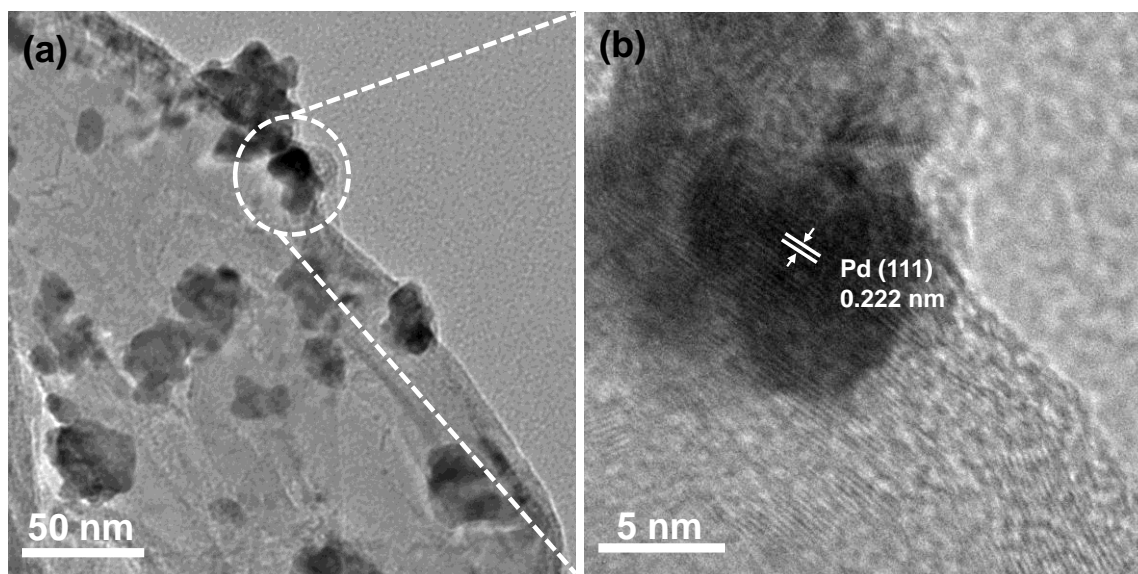


Figure S2. TEM and HRTEM images of Pd/CNTs catalyst.

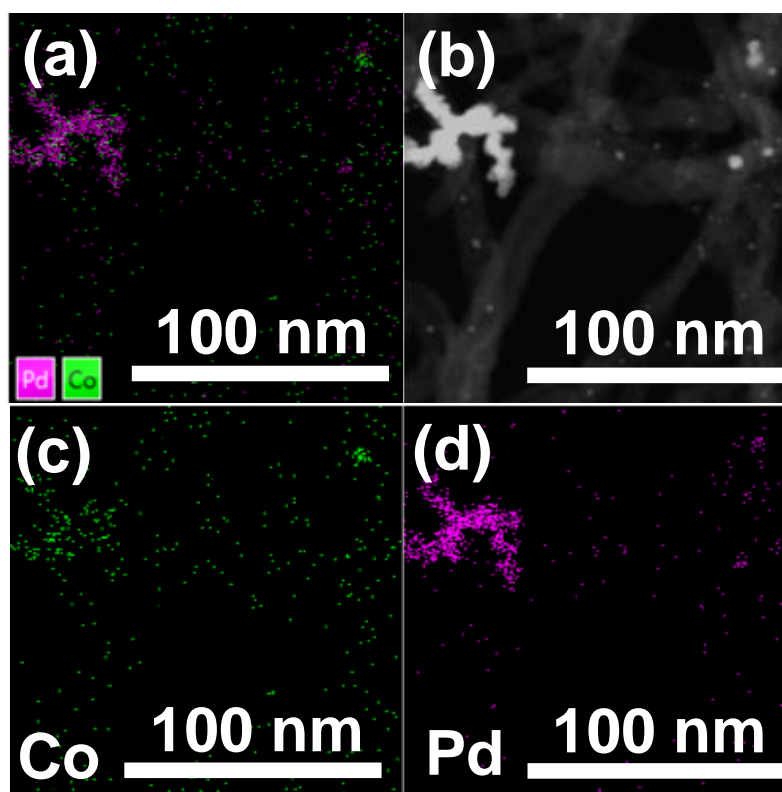


Figure S3. TEM and HRTEM images; HAADF-STEM elements mapping; the corresponding elements Pd and Co of $\text{Pd}_3\text{Co}_1/\text{CNTs}$ (another region).

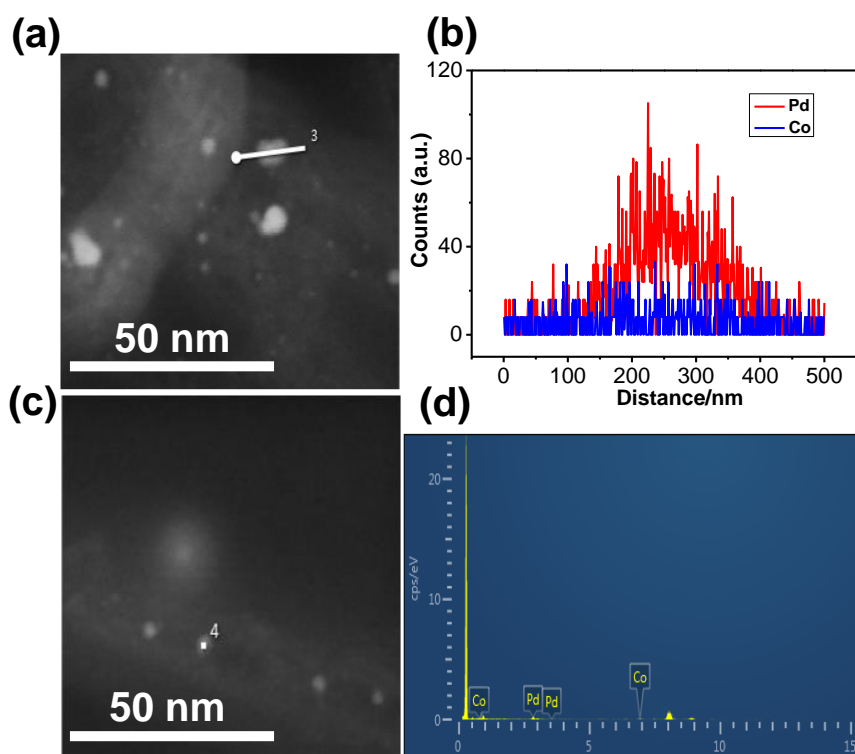


Figure S4. EDX line-profiles (a-b), spot scanning (c-d) of a Pd_3Co_1 nanoparticle

(where Pd is in red and Co in blue) of Pd₃Co₁/CNTs.

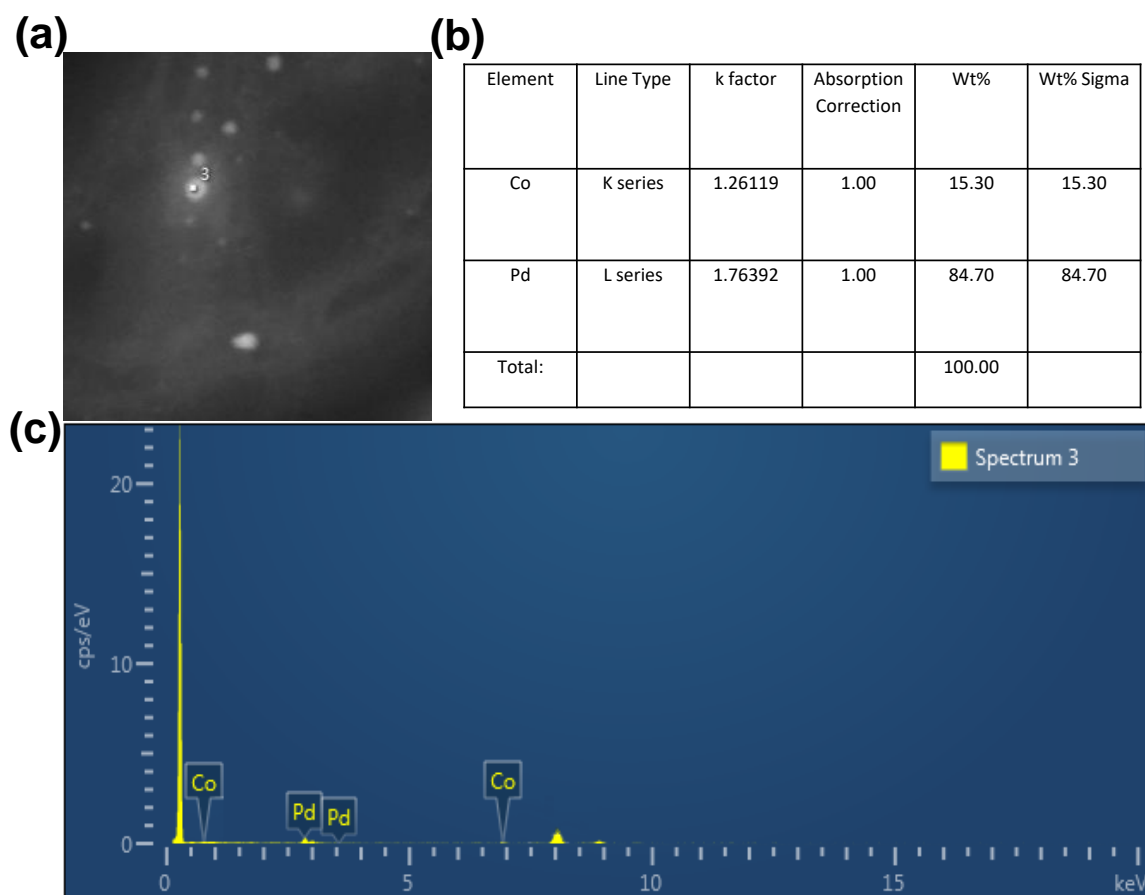


Figure S5. EDX-spot scanning (a) and element content ratio (b-c) of a Pd₃Co₁ nanoparticle in Pd₃Co₁/CNTs.

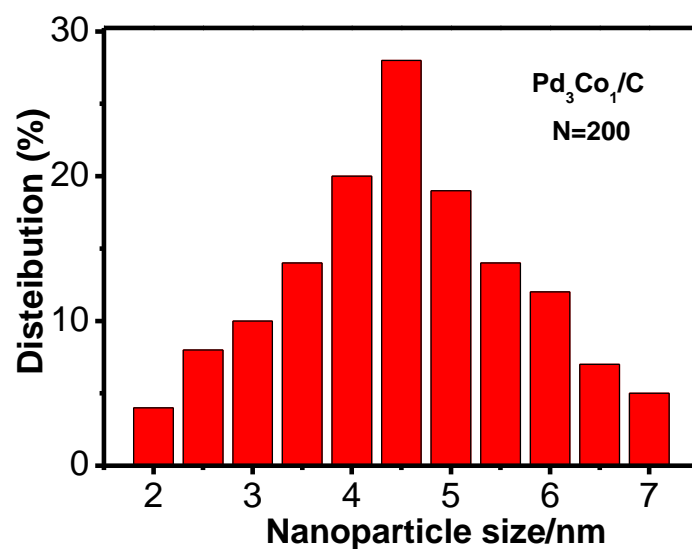


Figure S6. The corresponding particle size distribution of Pd₃Co₁/C catalyst.

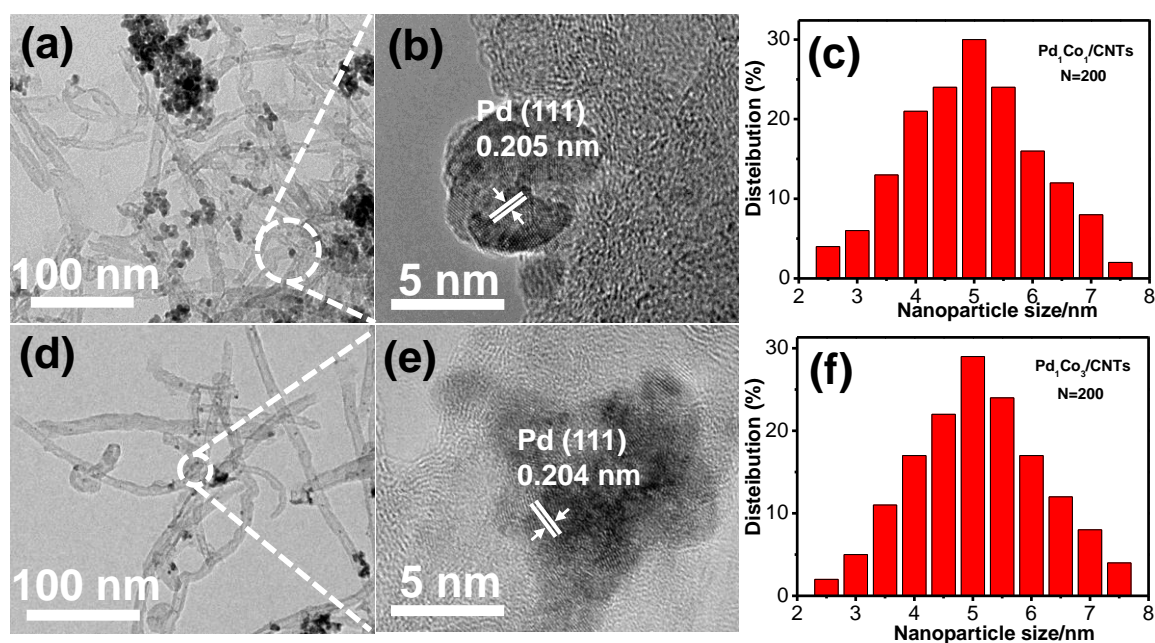


Figure S7. TEM and HRTEM images and the corresponding particle size distribution of Pd₁Co₁/CNTs (a-c) and Pd₁Co₃/CNTs (d-f) catalysts.

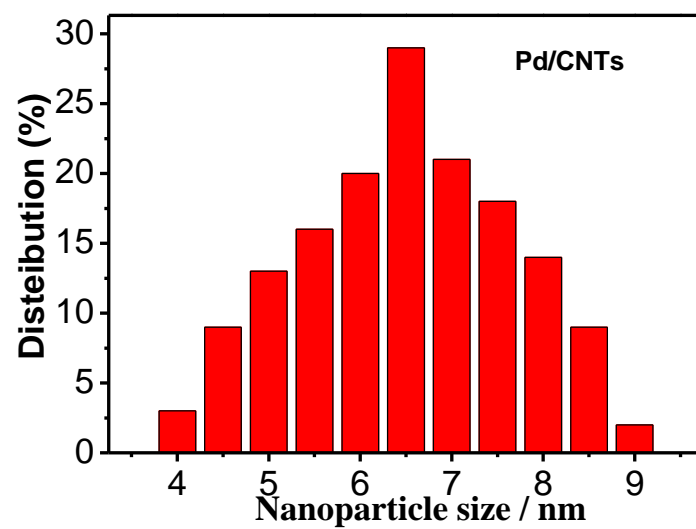


Figure S8. The corresponding particle size distribution of Pd/CNTs.

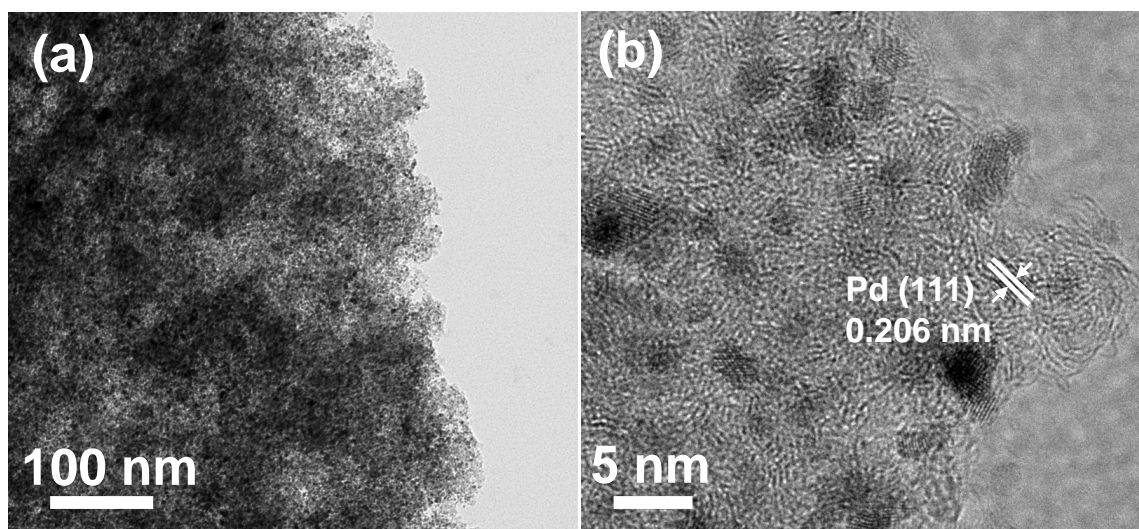


Figure S9. TEM and HRTEM images of Pd₃Co₁/C catalyst.

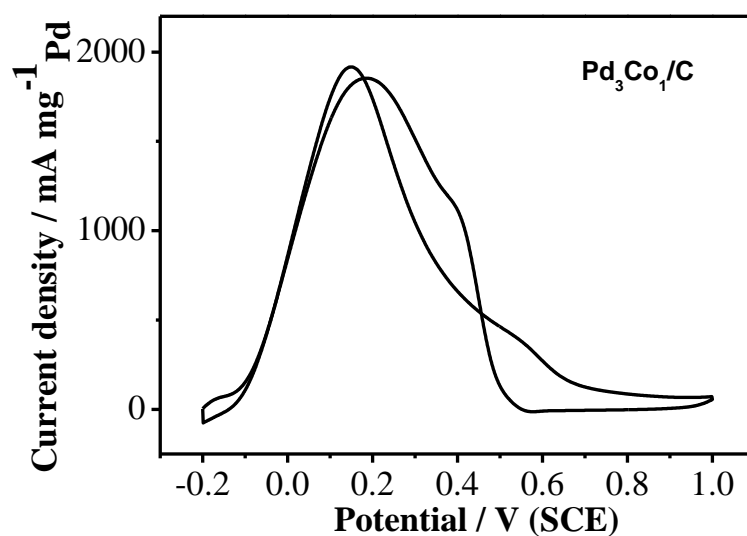


Figure S10 Cyclic voltammograms curve of Pd₃Co₁/C in 0.5 M H₂SO₄+1.0 M HCOOH.

Table S1. Elemental composition of the samples obtained from ICP.

| Elements Catalysts | Pd(wt.%) | Co(wt.%) | Atomic ratios |
|---------------------------------------|----------|----------|---------------|
| Pd ₃ Co ₁ /CNTs | 19.1 | 6.35 | 3:1 |
| Pd ₁ Co ₁ /CNTs | 18.3 | 17.9 | 1:1 |
| Pd ₁ Co ₃ /CNTs | 18.6 | 55.1 | 1:3 |
| Pd/CNTs | 17.5 | - | - |

Table S2. Pd 3d peaks of Pd₃Co₁/CNTs and Pd/CNTs.

| Catalysts | Pd ⁰ 3d _{5/2} (eV) | Pd ⁰ 3d _{3/2} (eV) | Pd ²⁺ 3d _{5/2} (eV) | Pd ²⁺ 3d _{3/2} (eV) |
|---------------------------------------|---|---|--|--|
| Pd ₃ Co ₁ /CNTs | 335.8 | 336.8 | 340.7 | 341.3 |
| Pd/CNTs | 335.5 | 336.2 | 340.6 | 341.1 |

Table S3 a recent literatures survey of the activity of FAOR electrocatalysts.

| Catalysts | Mass activity (mA mg ⁻¹ Pt) | References |
|---------------------------------------|--|------------|
| Pd ₃ Co ₁ /CNTs | 2410.1 | This work |
| PdCo nanodots | 1362.1 | [22] |
| PdCu nanochains | 1108.2 | [26] |
| PdCu clusters | 1289.0 | [57] |
| coral-like PdCu | 1050.0 | [61] |
| Pd ₆ Co nanocrystals | 430.8 | [62] |
| PdCu nanoparticles | 194.5 | [63] |
| (3D) porous PdSn | 553.4 | [64] |
| PdCu porous network | 517.0 | [65] |
| Pd-Fe nanoparticles | 1000.0 | [66] |
| PdCu/CNTs | 252.0 | [67] |