

Supporting information

Pd@TiO₂/Carbon Nanohorns electrocatalysts: Reversible CO₂ hydrogenation to formic

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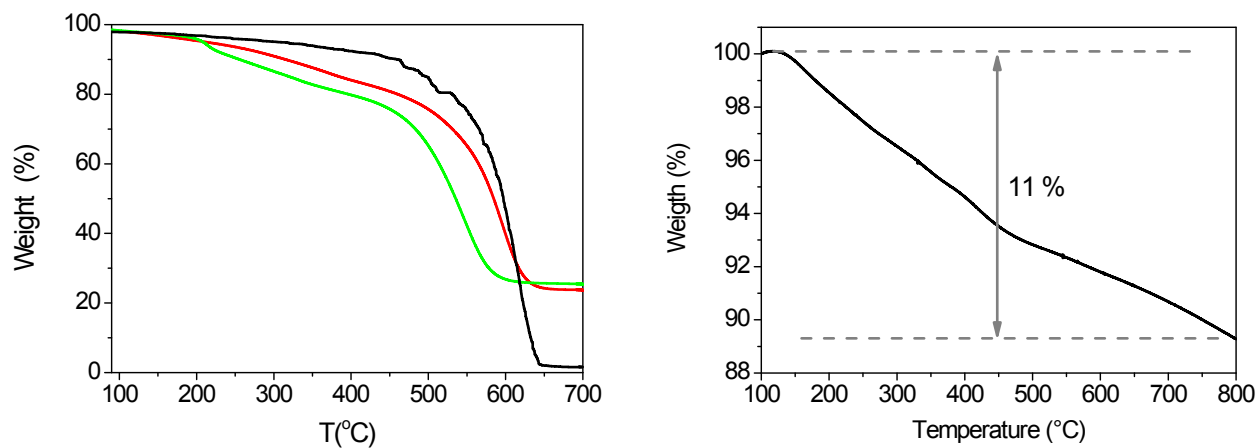


Figure S1. Left: O₂ - TGA plots of the (–) ox-SWCNHs, (–) TiO₂@ox-SWCNHs and the Pd@TiO₂/ox-SWCNHs (–) in air-atmosphere. Right: N₂ - TGA plot of ox-SWCNHs in N₂ atmosphere. The TGA analysis was performed on 1 mg of sample. The procedure included the equilibration at 100 °C for 20 min followed by a ramp of 10 °C min⁻¹ up to 800 °C.

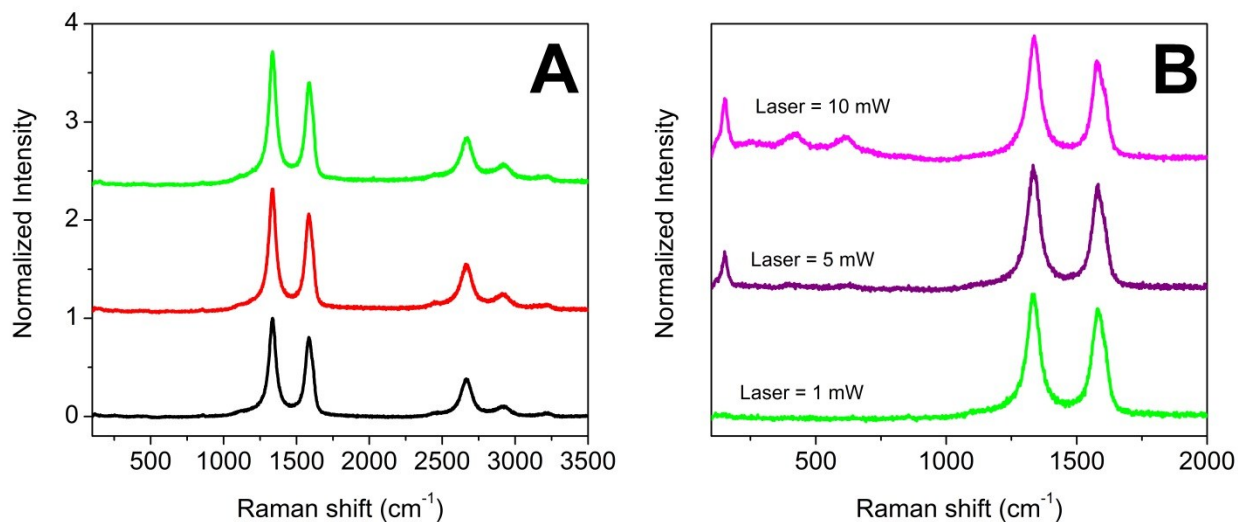


Figure S2. A) Raman spectra of the (–) ox-SWCNHs, (–) TiO₂/ox-SWCNHs and the Pd@TiO₂/ox-SWCNHs (–). B) Raman spectra of Pd@TiO₂/ox-SWCNHs at different laser powers, 1mW, 5 mW and 10 mW.

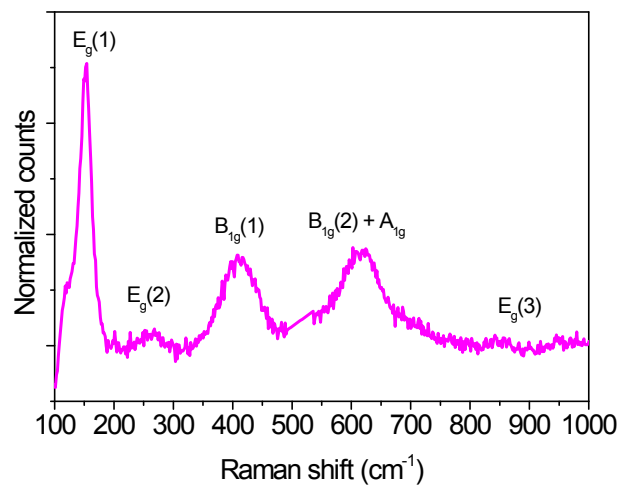


Figure S3. Raman spectra of the Pd@TiO₂/ox-SWCNHs at 10 mW.

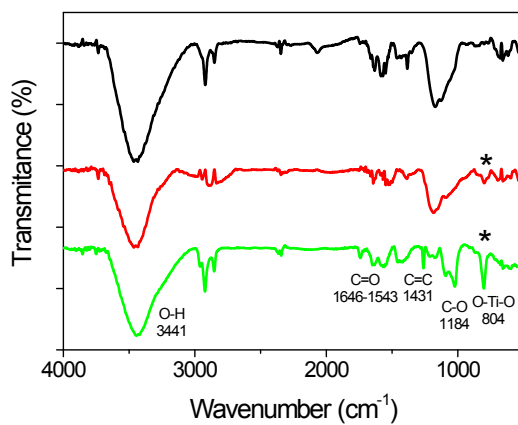


Figure S4. FT-IR spectra of (—) ox-SWCNHs, (—) TiO₂/ox-SWCNHs and Pd@TiO₂/ox-SWCNHs (—). * correspond to the signal of O-Ti-O vibration bond.

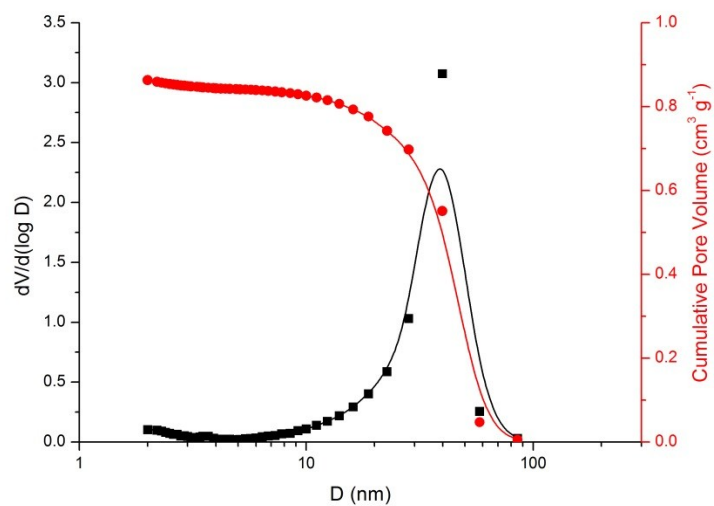


Figure S5. BJH pore size distributions calculated on the desorption branches for Pd@TiO₂/ox-SWCNHs.

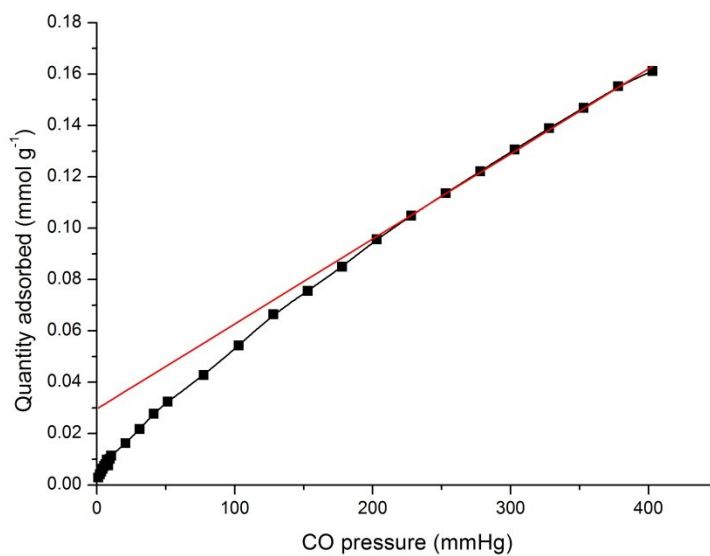


Figure S6. CO chemisorption isotherm of Pd@TiO₂/ox-SWCNHs.

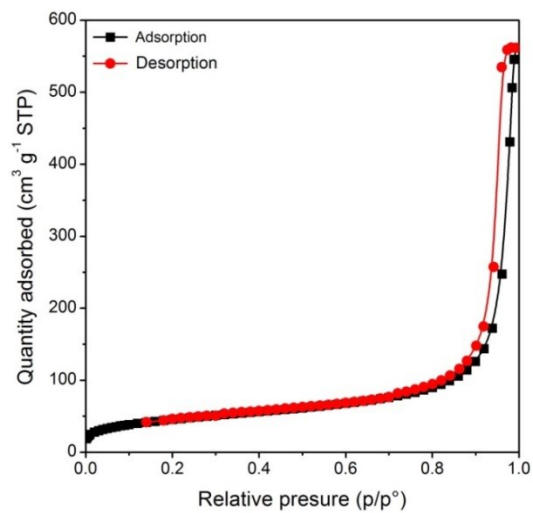


Figure S7. N_2 physisorption isotherm of Pd@TiO₂/ox-SWCNHs.

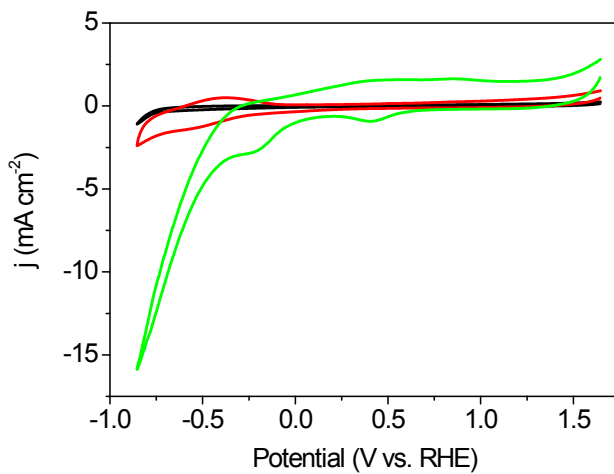


Figure S8. CVs obtained on GCE modified with ox-SWCNHs (-), TiO₂/ox-SWCNHs (-) and Pd@TiO₂/ox-SWCNHs (-) in 0.10 M phosphate buffer solution pH 7.40 under N_2 . Scan rate: 0.03 V s⁻¹.

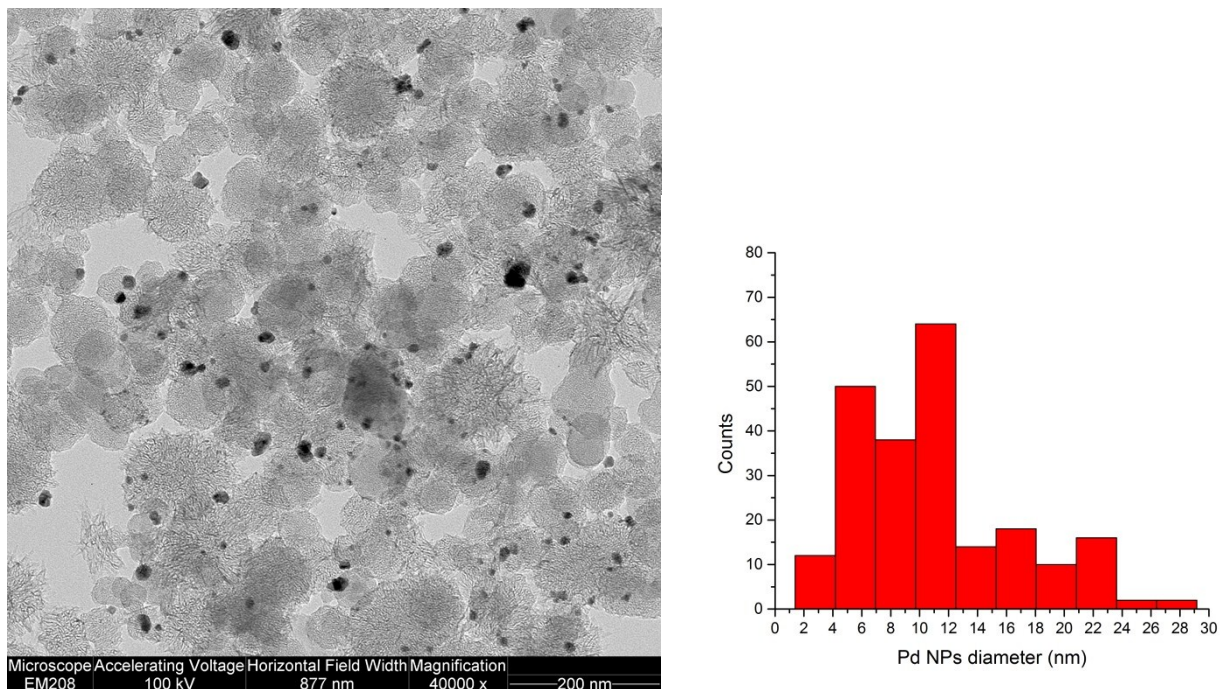


Figure S9. Left: Representative TEM micrograph of as-prepared Pd/ox-SWCNHs; right: Pd particle size dispersion

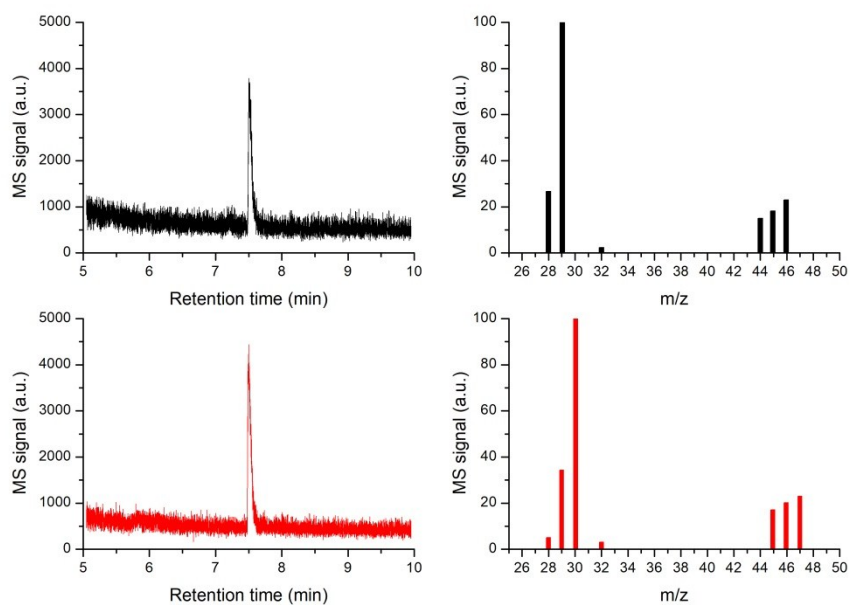


Figure S10. Gas chromatogram and corresponding mass spectrum of the electrolyte after chronoamperometry by Pd@TiO₂/ox-SWCNHs at -0.13V vs RHE under $^{12}\text{CO}_2$ (black) and $^{13}\text{CO}_2$ (red).

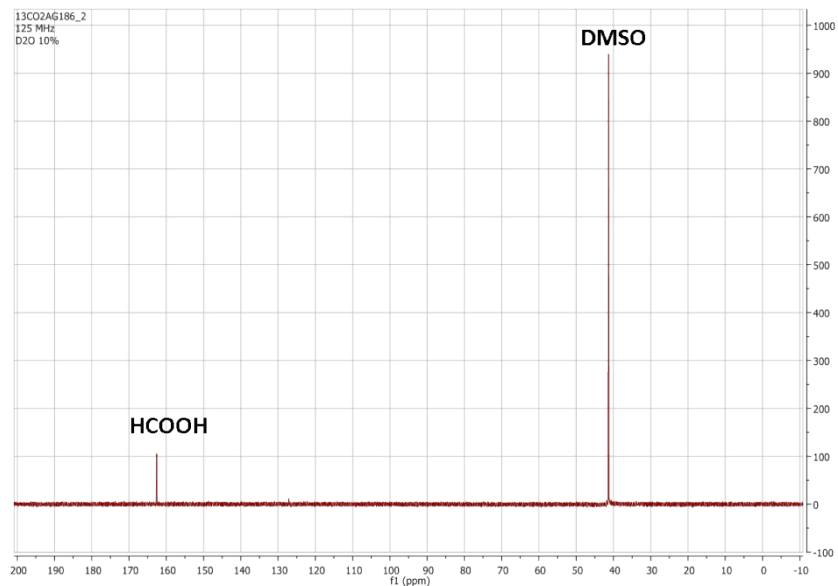


Fig S11. ^{13}C NMR spectrum of electrolyte after chronoamperometry of Pd@TiO₂/ox-SWCNHs at -0.2V vs RHE using $^{13}\text{CO}_2$. The NMR tube was prepared using: 500 μL of electrolytes, 100 μL D₂O and 50 μL DMSO as reference. Formic acid is identified with the C resonance peak at 164 ppm.

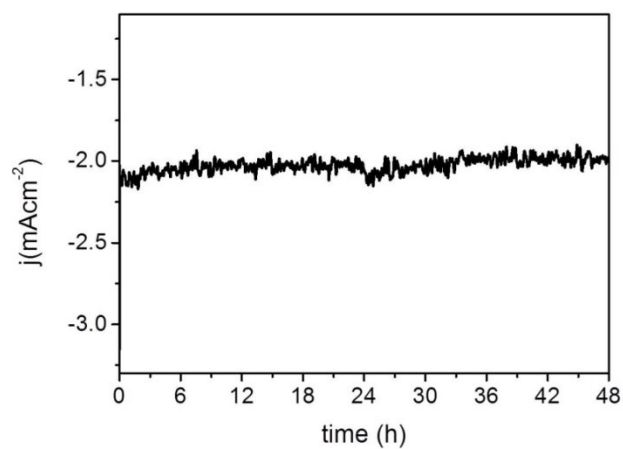


Figure S12. Current-time profile for Pd@TiO₂/ox-SWCNHs maintained at -0.2 V for 48 h. Supporting electrolyte: 0.10 M phosphate buffer solution pH 7.4. The Toray carbon electrode modified by drop casting using 200 μL 3.0 mg mL^{-1} Pd@TiO₂/ox-SWCNHs

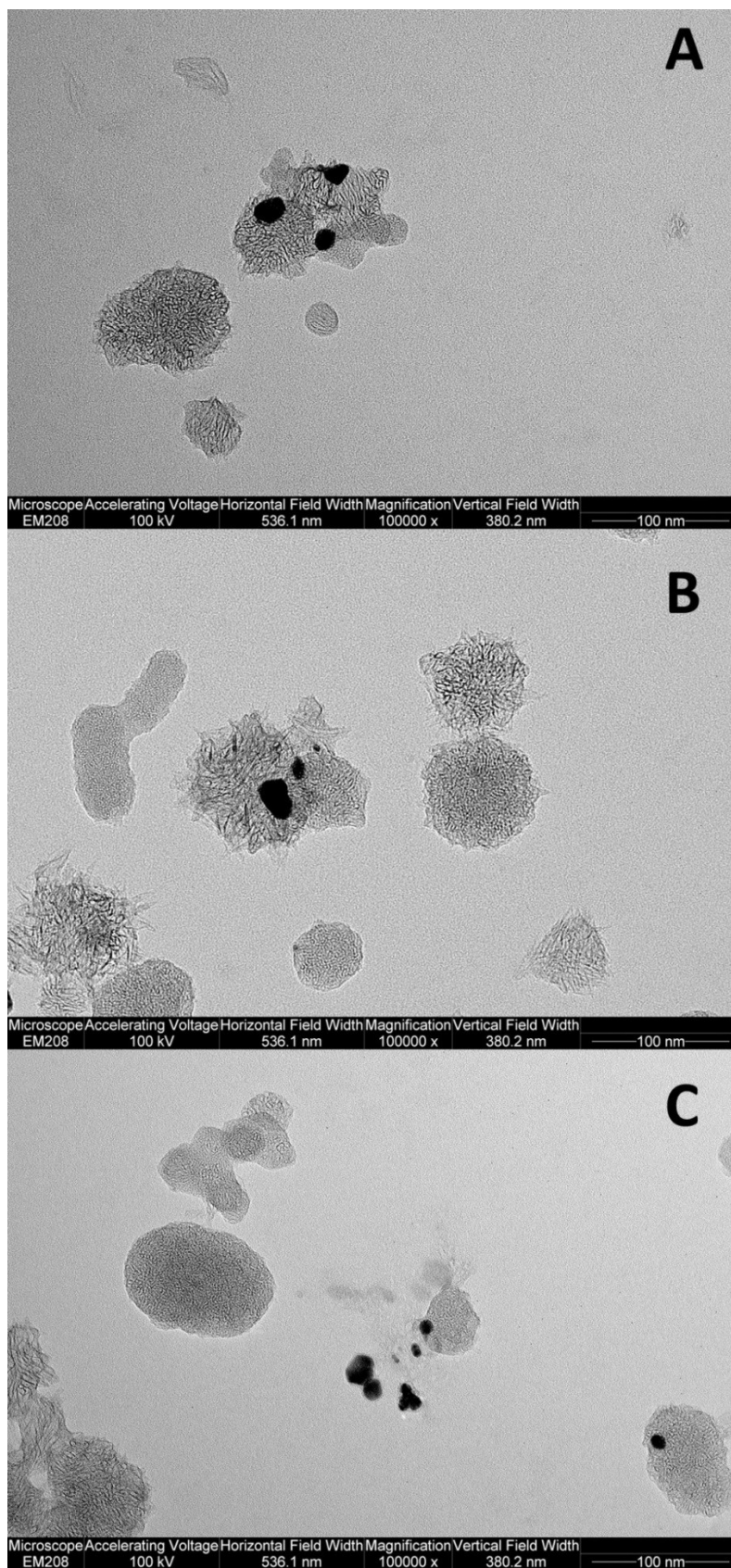


Figure S13. Representative TEM micrographs of Pd/ox-SWCNHs sample after 3h of electrocatalysis at -0.2 V showing agglomeration of the nanoparticles (A-B) together with some detachment from the SWCNHs (C).

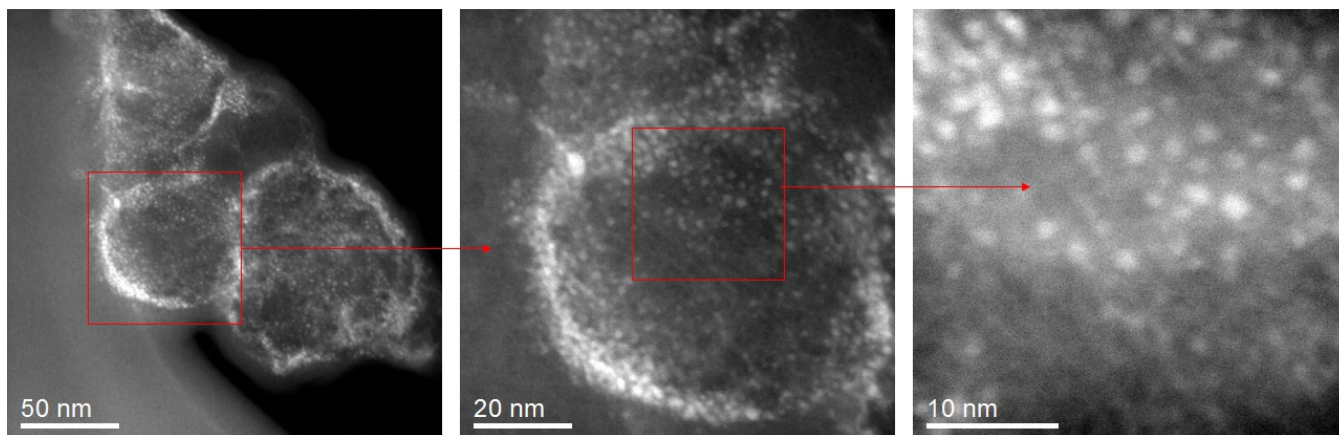


Figure S14. Representative HAADF-STEM of the catalyst Pd@TiO₂/ox-SWCNHs at different magnification: the bright spots are Pd NPs

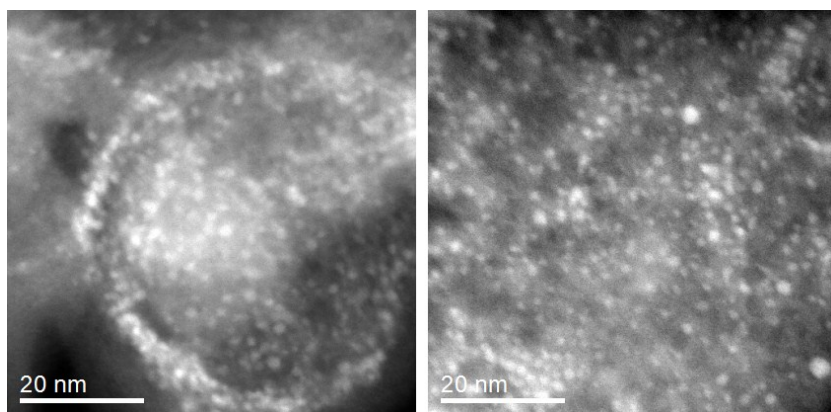


Figure S15. Representative HAADF-STEM at different magnification of the catalyst Pd@TiO₂/ox-SWCNHs post-catalysis showing no aggregation of the Pd nanoparticles

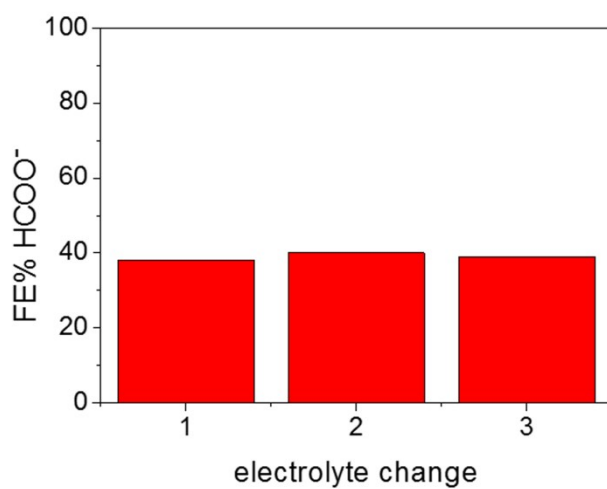


Figure S16. HCOOH FE% in function of the change of electrolyte NaClO₄ 0.5M. FE% were calculated over 1h of electrolysis at -0.13 V vs RHE.