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Direct electrooxidation of formic acid is of increasing interest as a potential liquid fuel for fuel cells.^[1] Carbon supported palladium is the typical catalyst and suffers from inefficient activity and poor stability.^[2] The present work was devoted to evaluation of a more active and durable catalyst. Tungsten carbide (WC) promoted palladium (Pd) and palladiumcobalt (PdCo) nanocatalysts are prepared and characterized for formic acid electrooxidation. The WC as the dopant to carbon supports is found to promote the activity of the Pd-based catalysts for formic acid oxidation. Alloying of Pd with Co further improves the electrocatalytic activity and stability of the WC supported catalysts, attributable to a synergistic effect of the carbide support and PdCo alloy nanoparticles.

WC was coated on carbon black by carbothermal synthesis at 900°C under N₂ atmosphere and the post treatment in NaOH solution was introduced for impurities removal.

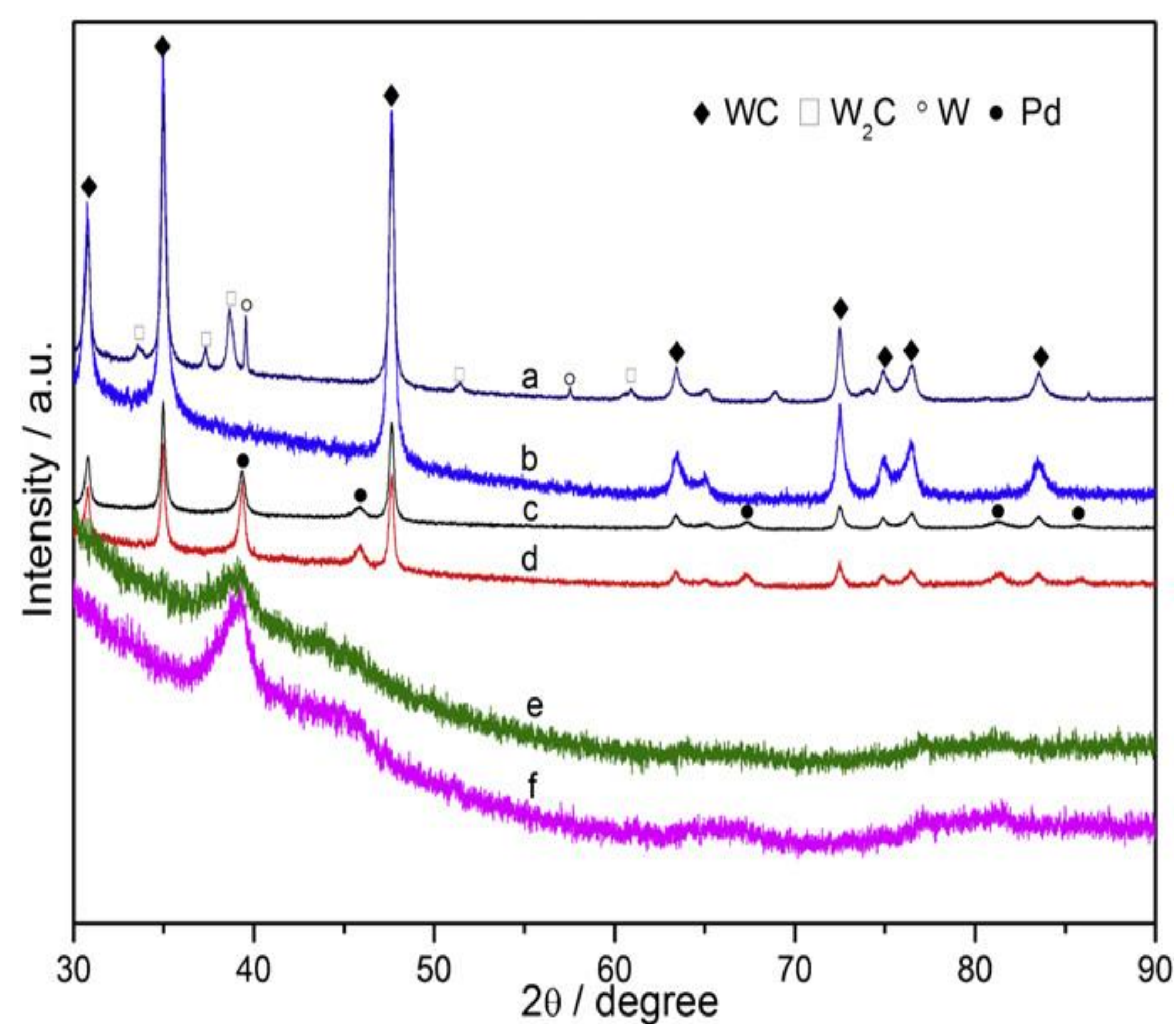


Figure 1. XRD for WC-C a) before and b) after NaOH treatment, c) Pd/C, d) PdCo/C, e) Pd/WC-C, and f) PdCo/WC-C samples.

The 3d_{5/2} binding energies of Pd species showed a shift from 336.0 for Pd/C to 336.1 for PdCo/C, 336.13 for Pd/WC-C and 336.27 eV for PdCo/WC-C, indicating the tunable Pd electronic properties by the metal-support interactions between Pd and WC.

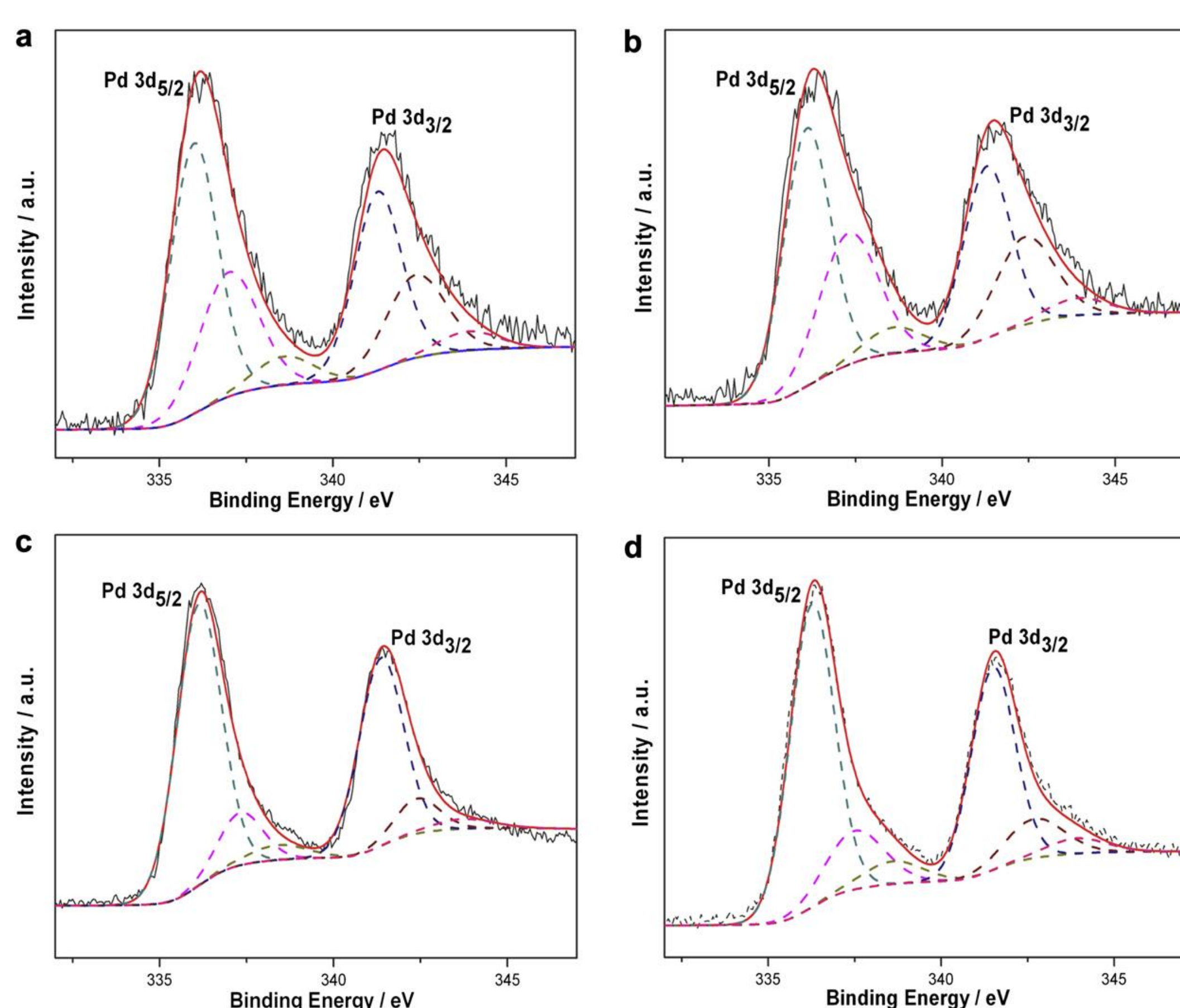


Fig. 3. XPS spectra of a) Pd/C, b) PdCo/C, c) Pd/WC-C, and d) PdCo/WC-C

The Pd and PdCo nanoparticles were dispersed uniformly on both carbon and WC modified carbon supports and had a rather narrow size distribution with an average particle size from 2.8 to 3.0 nm for all four types of catalysts. The modified WC at the surface of carbon with a diameter range from 6 to 10 nm. The metal nanoparticles and WC particles in a spherical shape overlay mutually at the surface of carbon.

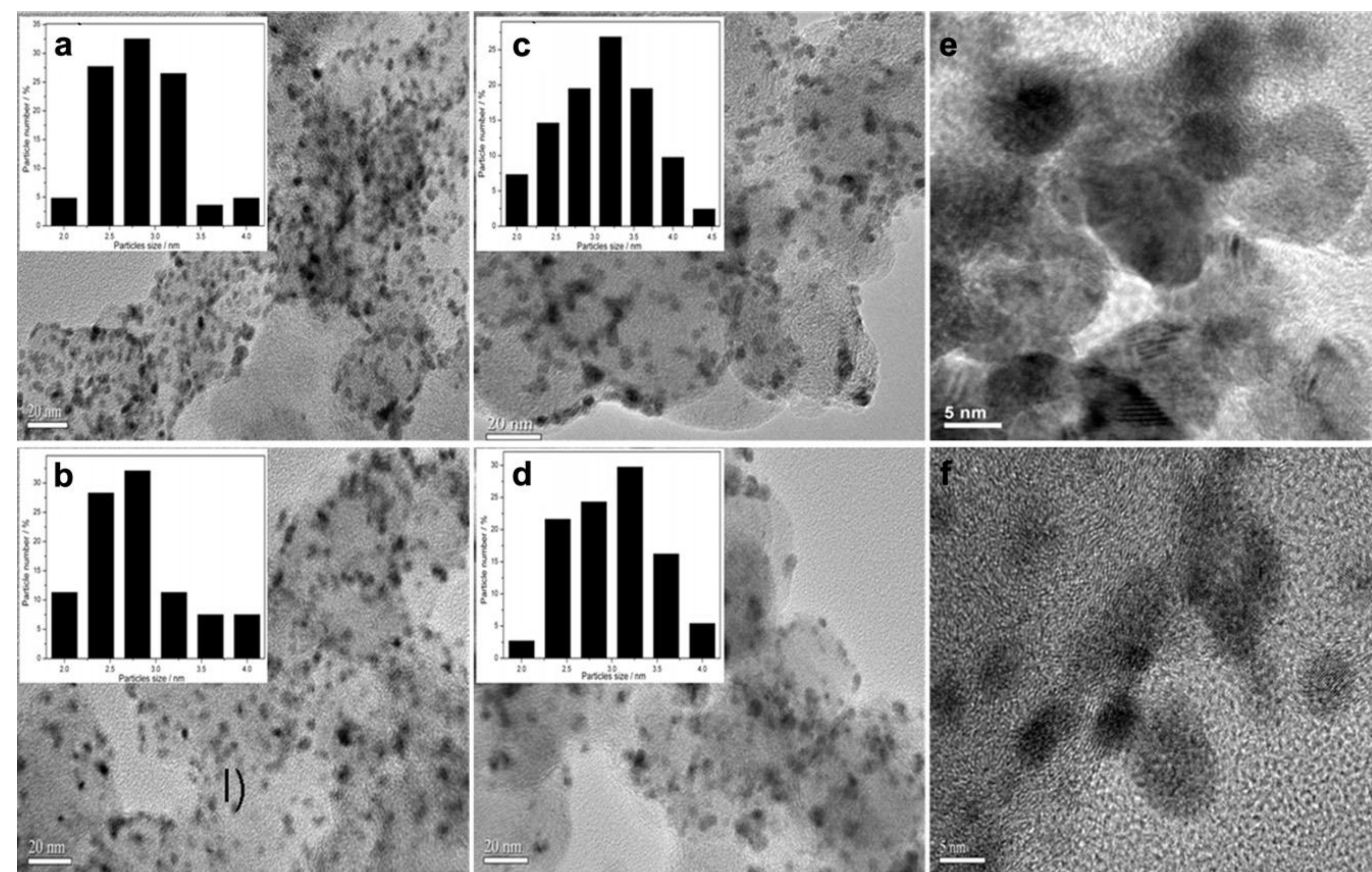


Figure 2. TEM images of a) Pd/C, b) PdCo/C, c) Pd/WC-C, and d) PdCo/WC-C and HRTEM images of e) WC-C and f) PdCo/WC-C. The insets in a), b), c), and d) are the corresponding particle size distribution histograms of each sample.

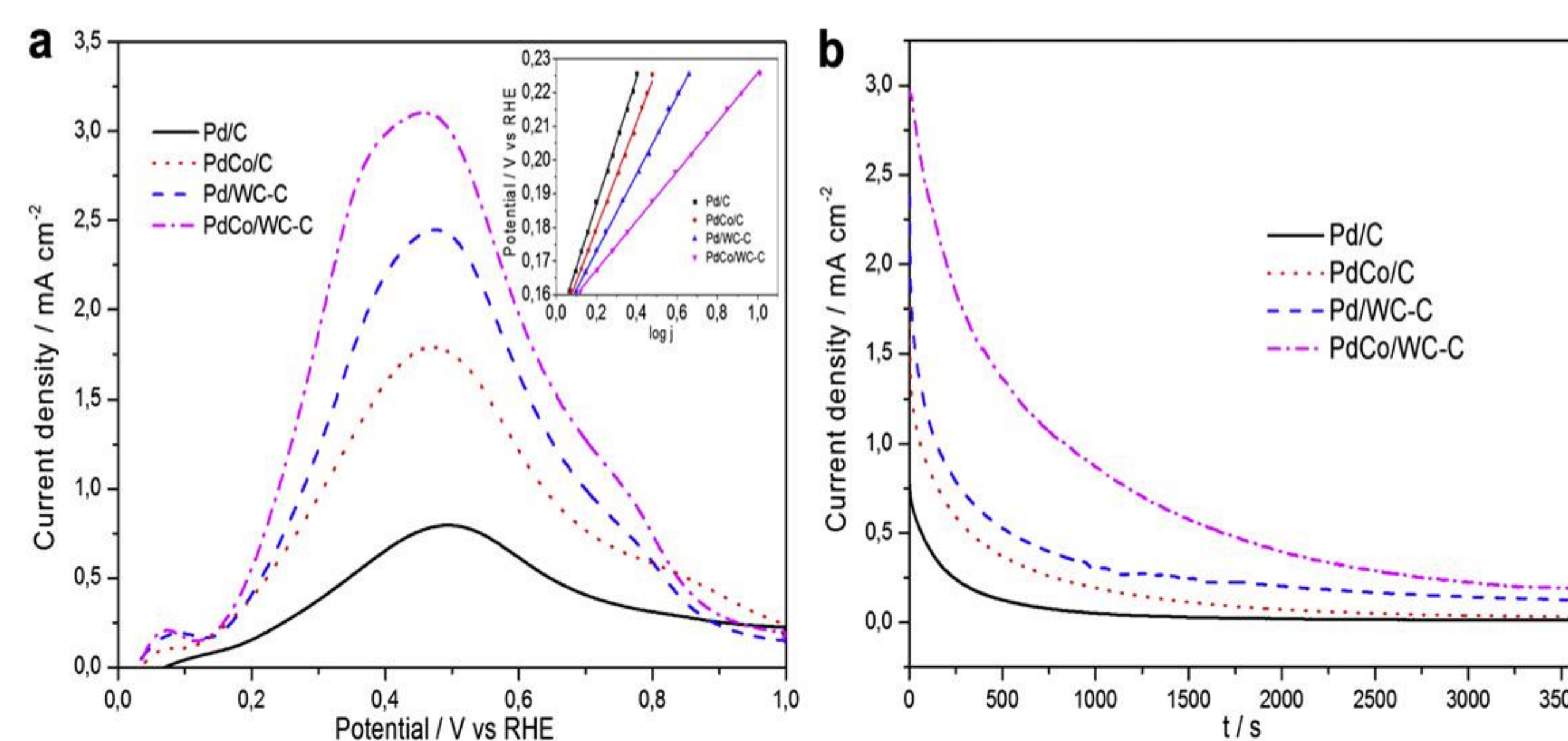


Fig. 4. a) CVs of each catalyst in N₂-saturated 0.5 M HCOOH + 0.5 M H₂SO₄ solutions at a scan rate of 50 mV s⁻¹. Inset: Tafel plots of each catalyst at a scan rate of 1 mV s⁻¹. The current (j) is normalized to the geometric electrode area. b) Amperometric i-t curves of HCOOH electro-oxidation on each catalyst in N₂-saturated 0.5 M HCOOH + 0.5 M H₂SO₄ at a fixed potential of 0.445 V vs RHE. The current density is based on the electrochemical surface area.

PdCo/WC-C showed the best catalytic activity and stability for formic acid oxidation. The synergistic effects among Pd, Co and WC were responsible for the improved performance.

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References

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- [2] X. W. Yu, P.G. Pickup, Electrochem. Commun. 11 (2009) 12.