Electronic Supplementary Information

Synergistic Effect of Tungsten Carbide and Palladium on Graphene for Promoted Ethanol Electrooxidation

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The preparation of graphene oxide

Graphene oxide (GO) was synthesized from expandable graphite according to a modified Hummers method. First, commercial expandable graphite was filtrated with an appropriate boult. Afterwards, expandable graphite was ground with sodium chloride, then washing away sodium chloride with water. The expandable graphite obtained was dried at 70 ℃ for 12 h. The dry solid was infused in 23 mL concentrated sulfuric acid in a beaker and stirred at room temperature for 24 h. 0.5 g of sodium nitrite was added into the suspension. After sodium nitrite entirely dissolved, 3 g of potassium permanganate was added into the beaker under an ice bath. The solution was maintained for 30 minutes at about 60 ℃ under a water bath. Then, 10 mL of distilled water was added into the solution. 5 minutes later, 100 mL of distilled water was added into the beaker and succeeding 10 mL of 30 % H_2O_2 was added into the reaction system. The yellow suspension obtained was filtrated and washed with diluted HCl solution, then washed repeatedly with distilled water finally. The obtained solid was dried at 70 ℃ for 48 h in oven.

Table S1 Calculated adsorption energies and layer charge variations for Pd-WC system.

$E_{bind.}$（J/m^2）	Δe(Pd)	Δe(W)	Δe(C)
-7.9651	-0.11 e	0.20 e	-0.01 e

Variations of layer charge (in e) due to the adsorption. Δe (Pd) denote value of the three Pd layers in the interface, Δe (W) and Δe (C) denote values of the first W and C layers that contact the Pd surface. The charge variation is the difference between surface and interface atomic charges, which were calculated according to the Mulliken method [Mulliken, R. S. *J. Chem. Phys*. **1955,** *23*, 1833-1846].

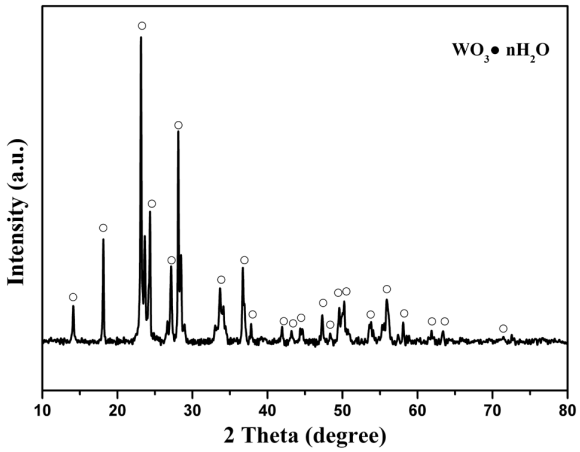

Fig. S1 XRD pattern of WO_3-nH_2O/GN.

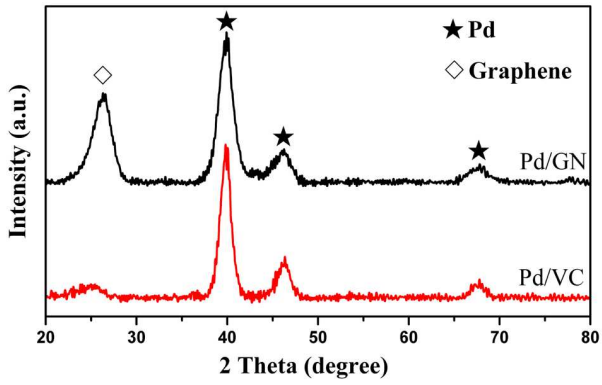

Fig. S2 XRD patterns of Pd/GN and Pd/VC.

$$WO_3\ (Hexagonal) \xrightarrow{transformation} WO_3\ (Orthorhombic)$$

$$WO_3\ (Orthorhombic) + C \longrightarrow WO_xC_y + CO/CO_2$$

$$WO_xC_y + C \longrightarrow W_nC_m + CO/CO_2$$

$$W_nC_m \longrightarrow W_2C + WC + W$$

$$W_2C + C \longrightarrow WC$$

$$W + C \longrightarrow WC$$

Fig. S3 Some reactions during the conversion phase from WO_3/GN to WC/GN.

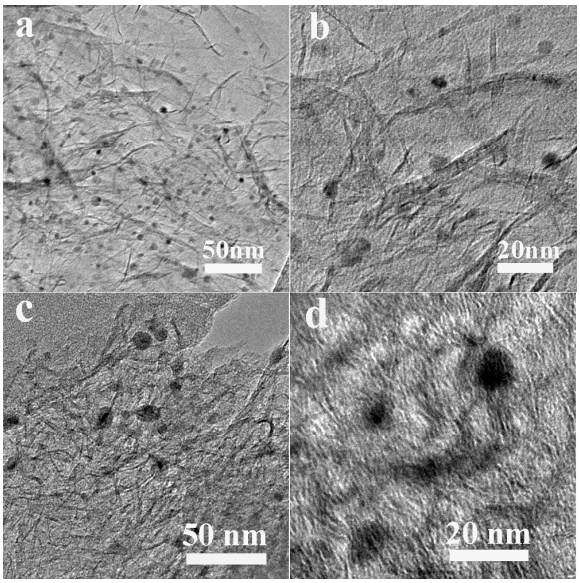

Fig. S4 Low and high magnification TEM images of (a, b) the WO_3-nH_2O/GN sample (before thermal treating) and (c, d) the WC/GN sample (after thermal treating).

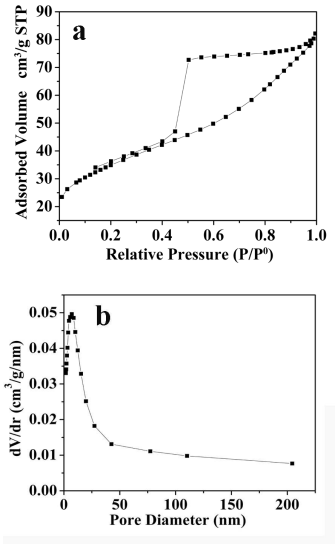

Fig. S5 Nitrogen adsorption/desorption isotherms of WO_3-nH_2O/GN sample. (The S_{BET} of WO_3-nH_2O/GN is 123.8 m^2/g).

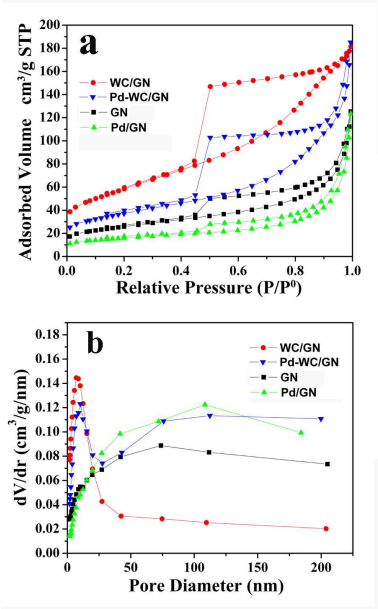

Fig. S6 (a) Nitrogen-sorption isotherms and (b) the corresponding pore-size distribution curves of different samples.

Table S2 The BET specific surface areas (S_{BET}) of the different samples.

Sample	S_{BET} (m^2/g)
GN	91.4
WC/GN	207.6
Pd/GN	56.2
Pd-WC/GN	131.9

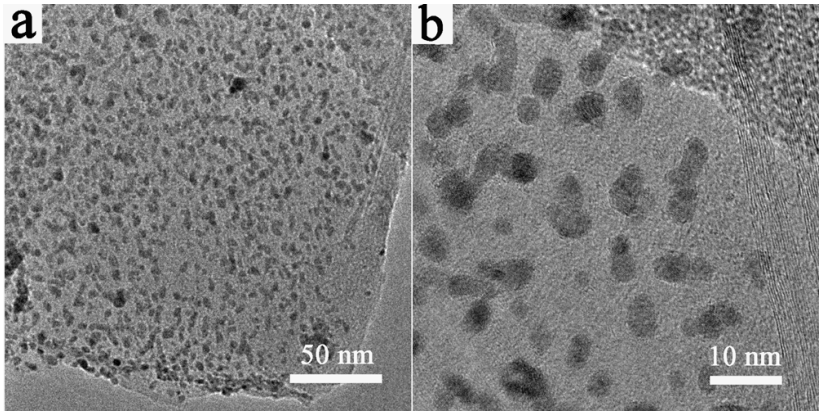

Fig. S7 (a, b)TEM images with different magnifications of Pd/GN sample.