Electronic Supplementary Information (ESI)

WC@*meso*-Pt core-shell nanostructures for fuel cells

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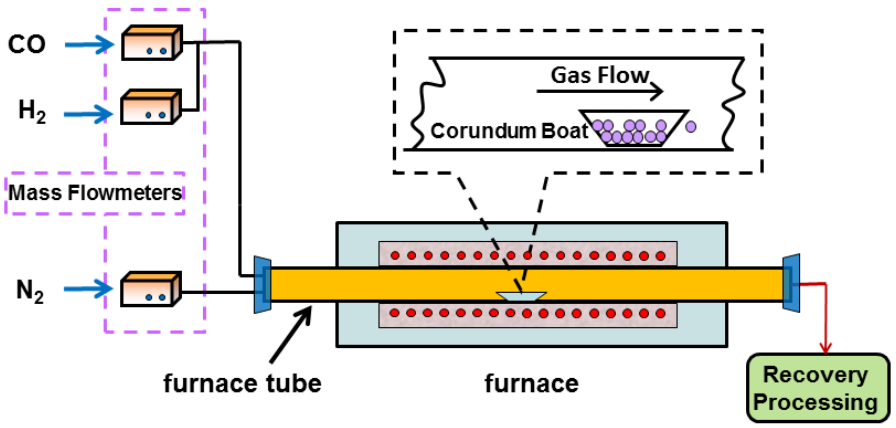

Figure S1. Schematic diagram of the setup used for the gas-solid reaction for the synthesis of WC@Cu.

Experimental details

A mixture of ammonium meta tungstate (AMT, $(NH_4)_2W_4O_{13}\cdot xH_2O$) and $Cu(NO_3)_2\cdot 3H_2O$ (W/Cu wt: 4:1) was added to de-ionized water at 17 weight percent. It was then treated by spray drying (BÜCHI Spray Dryer B-290) to produce microsized spherical precursor. During the drying process in a spray desiccator, the rate of hot air flow was 35 $m^3\ h^{-1}$, the temperature of the air at the nozzle was 185 ºC; the rate of evaporation of aqueous solution was 15 ml min^{-1}, and the temperature of the mixture of gas and powder at the exit was 92~95 ºC. This sample underwent the gas-solid reaction (Figure S1) under an atmosphere of CO/H_2. The flow rates of CO and H_2 were 125 $cm^3\ min^{-1}$ and 250 $cm^3\ min^{-1}$, respectively. Initially, furnace temperature was raised to 400 °C and maintained for 1 h after the reaction zone was free from oxygen. Thereafter, the temperature was raised to 800 °C and maintained for 4 h. The sample was cooled to room temperature at the end of the reaction. Replacement of the Cu by Pt was carried out in H_2PtCl_6 solution (5 mmol L^{-1}, 10% Pt loading) at 50 °C for 6 h. The electrocatalytic properties of the WC@Pt were analyzed by employing the powder micro electrode (PME, 60μm in diameter) approach at room temperature. The structure and preparation of the PME have been described previously.[1] The WC@*m*-Pt sample was ground and inserted into the lower tip of the electrode.[2] Cyclic voltammetry of WC@Pt was carried out using an electrochemical station (CHI-

660c), where oxidation current is defined as positive current. Each stage contains 5 cycles. Pt foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively.

The phases present in the synthesized material was identified using XRD (Panalytical X'Pert Pro, Cu Kα1 radiation source (λ=0.1541 nm), voltage of 40 kV, current of 40 mA). The morphology and structure of the products were characterized using FE-SEM (Hitachi S-4700 II, using carbon conductive adhesive) and TEM (Tecnai G2 F30, Ni grid) and HR-TEM with EDS. The specific surface area of the sample pores were measured by nitrogen adsorption-desorption analyse (Micromeritics ASAP 2020).

1. C. A. Ma, J. F. Sheng, N. Brandon, C. Zhang, G. H. Li, Int. J. Hydrogen Energy 2007, 32, 2824.
2. C. Cachet-Vivier, V. Vivier, C. S. Cha, J.-Y. Nedelec, L. T. Yu, Electrochim. Acta. 2001, 47, 181.

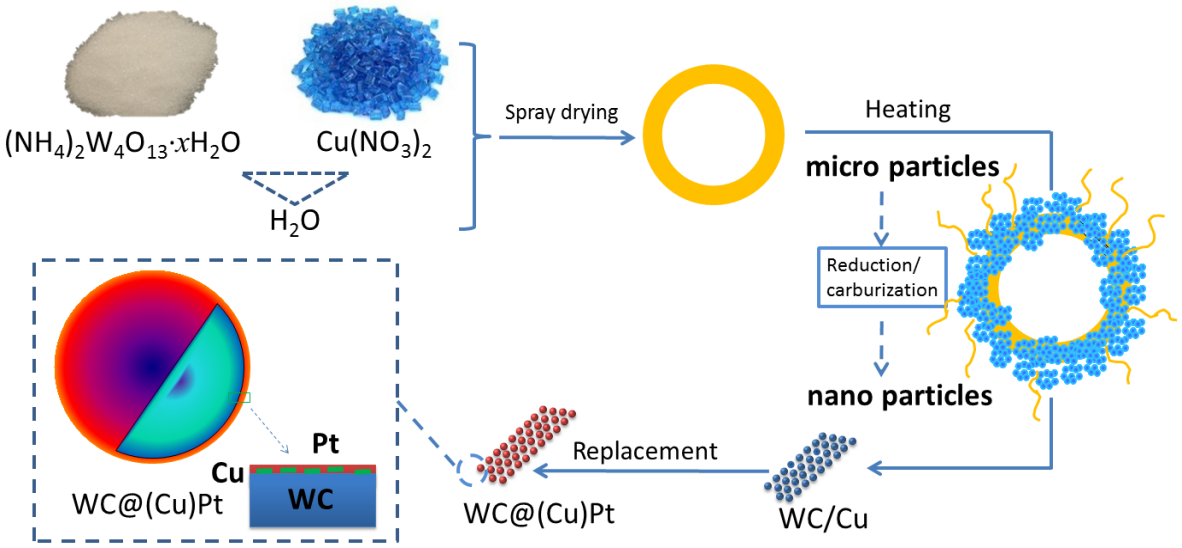

Figure S2. Schematic of the synthesis process of core-shell WC@(Cu)Pt.

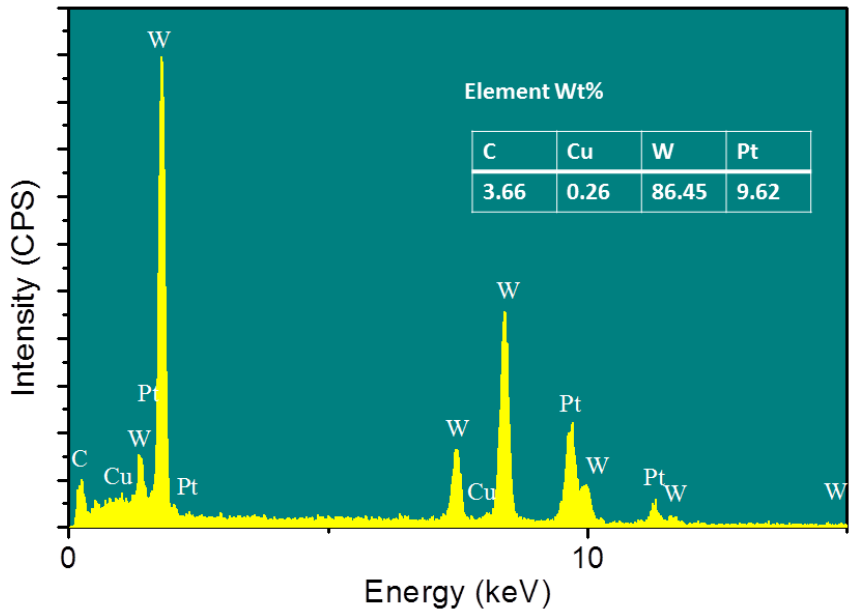

Fig. S3. Energy dispersive X-ray spectroscopy (EDS) spectrum and the elemental analysis of the WC@(Cu)Pt sample.

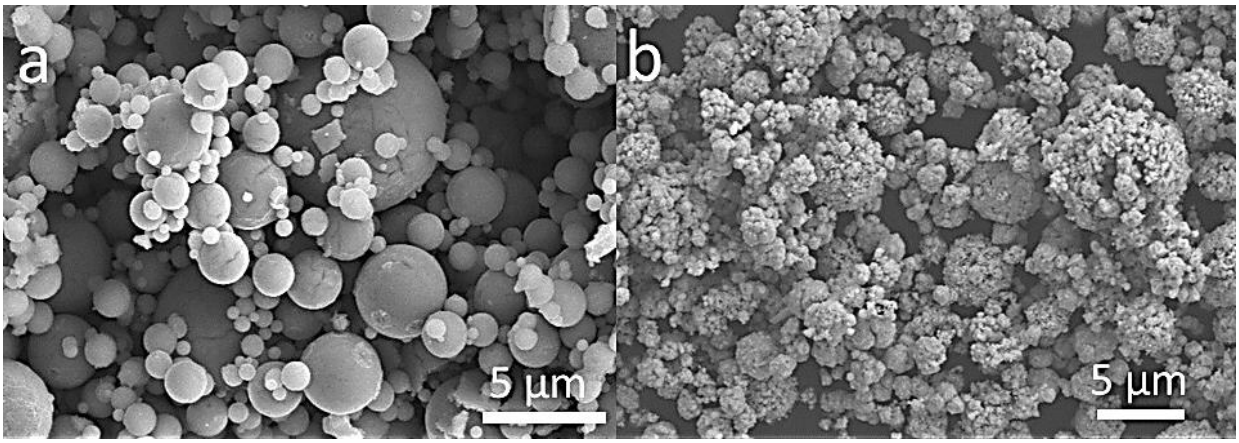

Fig. S4. SEM images for the presursor (a) and the resultant sample (b) of a parallel experiment without the addition of copper nitrate**.**

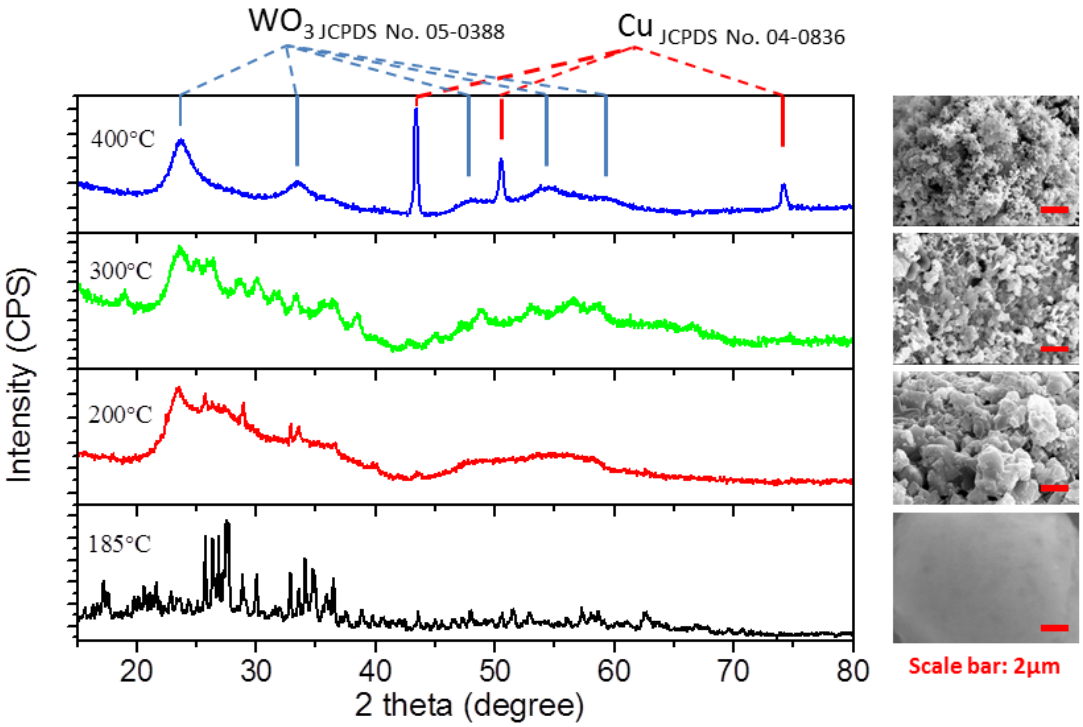

Fig. S5. XRD patterns and SEM images of the sample taken out at different temperatures during the heating process.

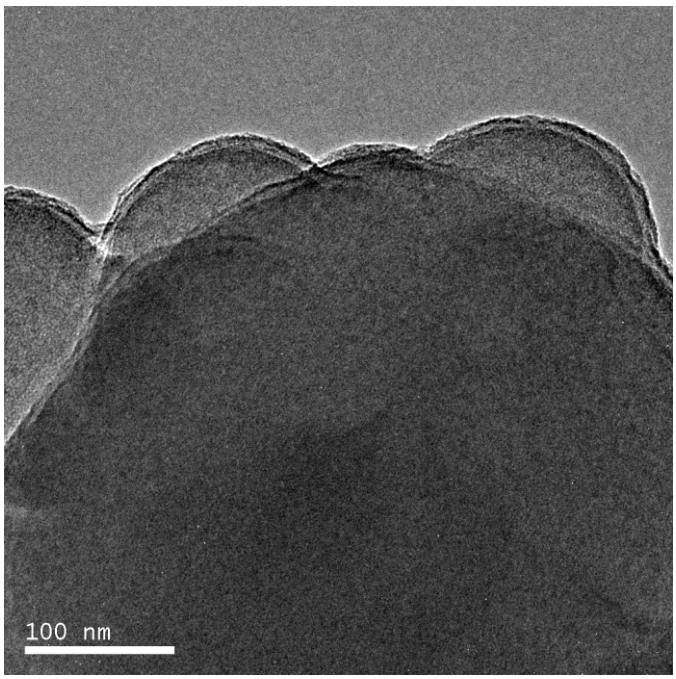

Fig. S6. TEM image of the sample taken out at 210 ℃ during the spray drying process.

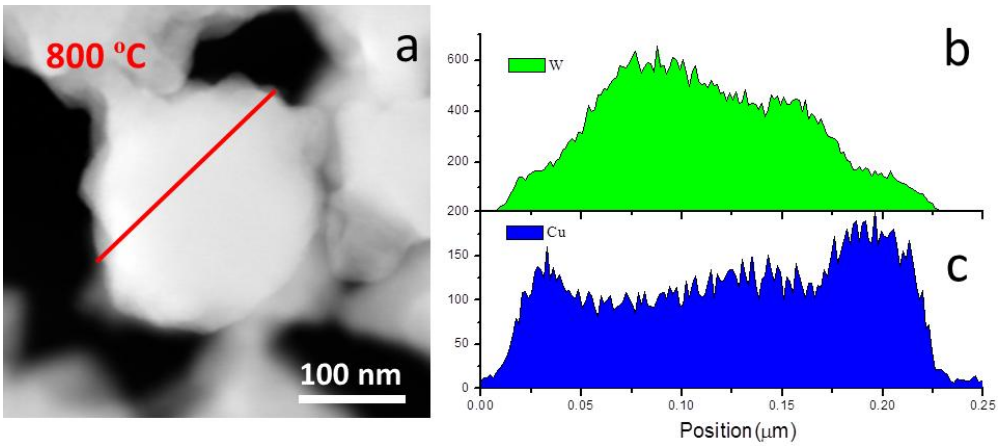

Fig. S7. (a) TEM image of the sample taken out at 800 ℃during the heating process/gas-solid reactions, and (b and c) the corresponding EDS line-scan analysis of the profiles of W and Cu along the selected line across a sample particle.

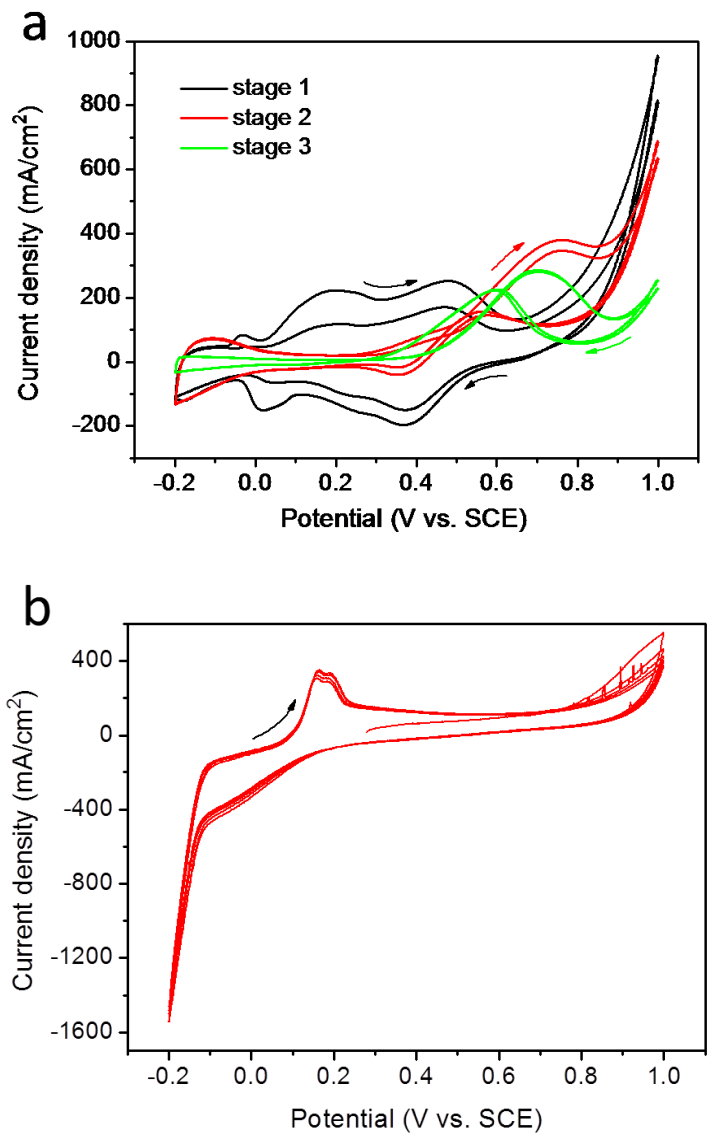

Fig. S8. (a) CVs showing the 3 stages of WC@(Cu)Pt in 2M CH_3OH + 1M H_2SO_4 solution with a scan rate of 50mV s^{-1} at 25°C; (b) the CVs of WC@Cu cycled 5 times under the same conditions.

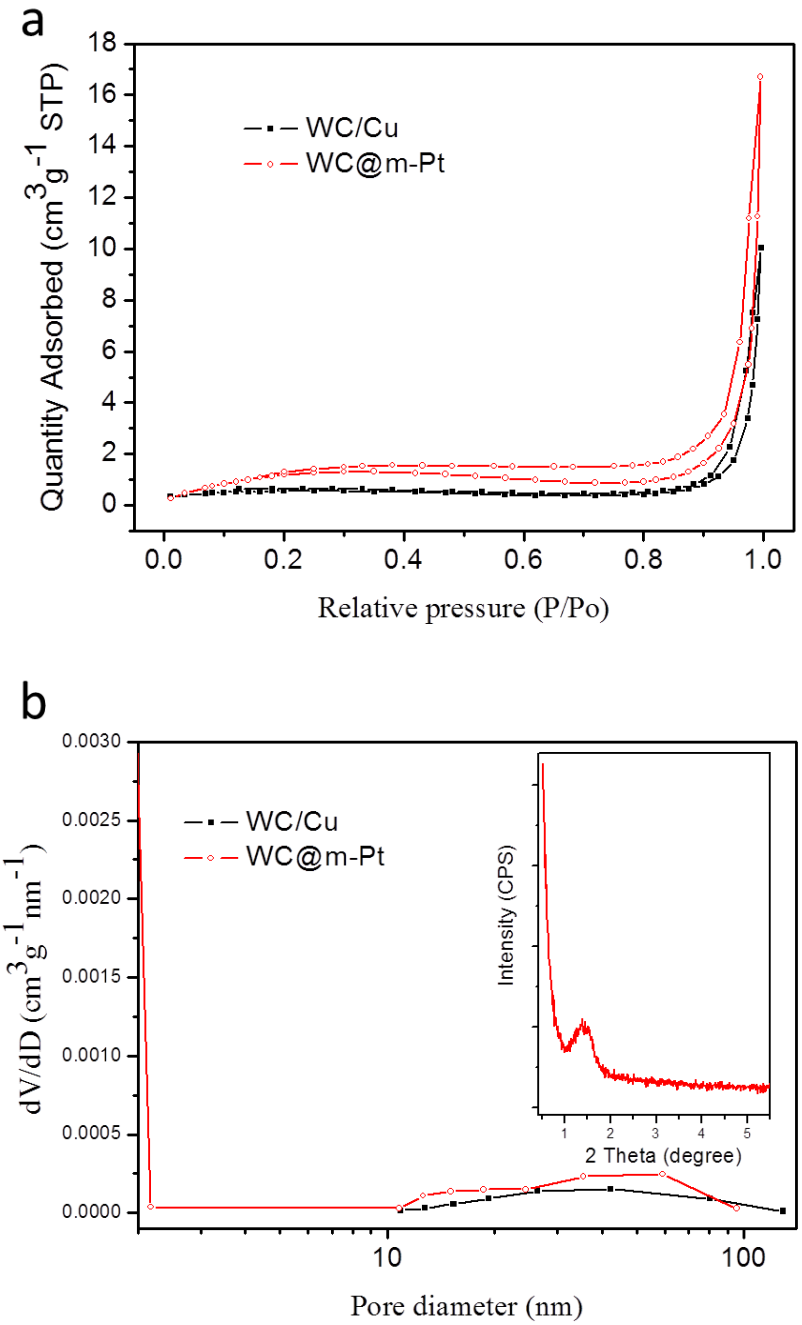

Fig. S9. (a) N_2 sorption isotherms and (b) the corresponding pore-size-distribution curves of WC/Cu and WC@*m*-Pt (inset is the small-angle XRD pattern of WC@*m*-Pt).