Supporting Information

In-situ fabrication of rose-shaped $Co_2P_2O_7$/C nanohybrid via coordination polymer template for supercapacitor application

Jiaxin Zhang, Peng Liu, Ranran Bu,, Hao Zhang, Qi Zhang, Kang Liu, Yanru Liu, Zhenyu Xiao*, Lei Wang*

Key Laboratory of Ecochemical Engineering, Taishan Scholar Advantage and Characteristic Discipline Team of Ecochemical Process and Technology, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China.

Containing: 9 pages, 12 Figures, 5 equations and 1 Table

1. Electrochemical measurements

The electrochemical behaviors are carried out by a CHI 760E electrochemical station in 6 M KOH. In the three-electrode system, we use a platinum wire (0.5 cm × 37 mm) as the counter electrode and a Hg/HgO electrode as the reference electrode. For the working electrode, we prepare a homogeneous slurry, containing 80 % active materials, 10 % carbon black, and 10 % polytetra-fluorethylene (PTFE) in ethanol. After drying at 70 °C for 12 h, weighing about 2.5 mg of the solidified mixture and then pressed between two pieces of nickel foam (1 cm × 2 cm) under 1.0 MPa.

An all-solid-state hybrid supercapacitor is assembled by using active materials ($Co_2P_2O_7$/C-900) as the positive electrode, 3DPG as the negative electrode, and PVA/KOH hydrogel polymer as the electrolyte. The negative electrode contains 3D porous graphene, carbon black and PTFE with a weight ratio of 8:1:1. The PVA/KOH gel electrolyte is synthesized by a common way: 1 g PVA is added into 40 mL of H_2O with heating and stirring to form a clear solution; then 6 g of KOH is added into the solution and dried in the air to obtain the PVA/KOH gel electrolyte.

2. Characterization:

All chemicals are analytical grade and were used without any purification. Powder X-ray diffraction patterns of the prepared samples are collected on a Rigaku D-MAX2500/PC advance instrument with Cu-Kα radiation (λ = 1.5418 Å). The XPS spectrum of $Co_2P_2O_7$/C-900 is measured by Thermo Scientific 250xl. The morphology and structure of the prepared samples are examined by electron microscopy (SEM, Zeiss merlin; TEM, FEI Tecnai G^2 F20). The Thermogravimetric analysis (TGA) is recorded by TA STA Q600 (U.S.A.) in N_2. The Raman spectra are recorded on a LabRRM HR Evolution instrument with the excitation light (Ar^+ laser, 633 nm). The N_2 adsorption−desorption isotherms at 77 K is tested by a Quantachrome instruments version 4.01.

3. Characterization

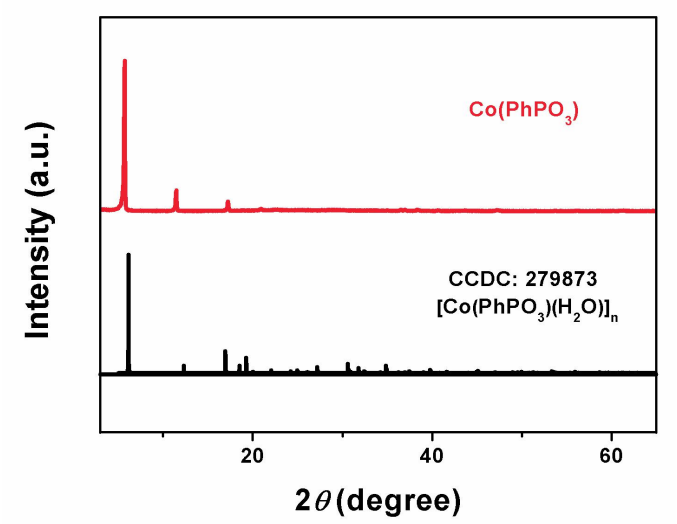

Figure S1. The PXRD patterns of $Co(PhPO_3)$ and $[Co(PhPO_3)(H_2O)]_n$.

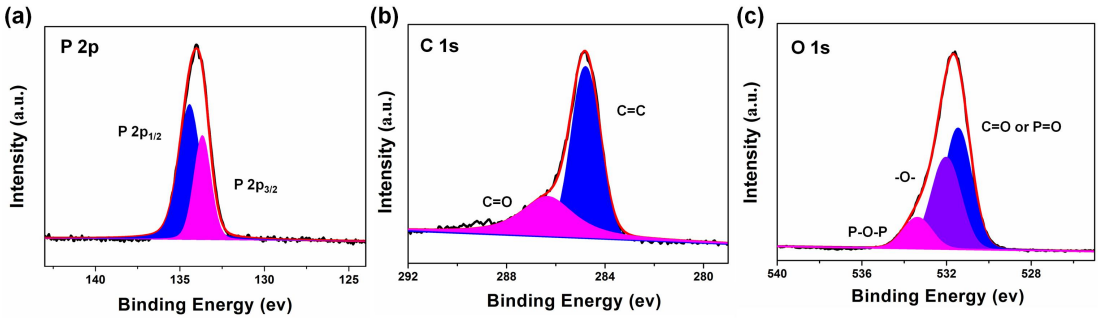

Figure S2. The P 2p spectra (a), C 1s spectra (b) and O 1s spectra (c) of $Co_2P_2O_7$/C-900.

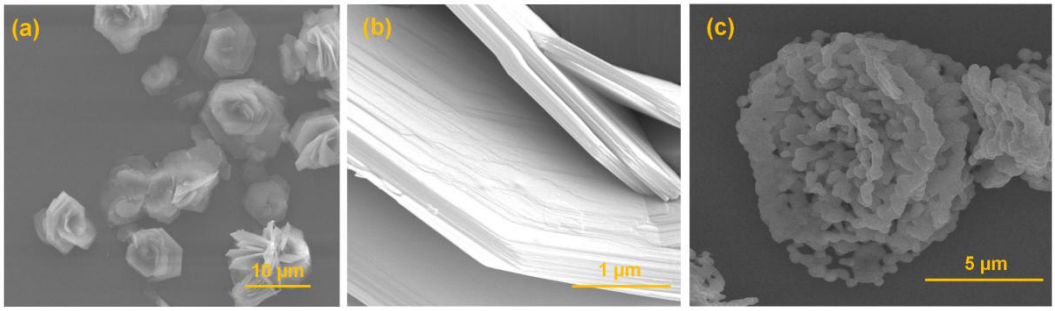

Figure S3. The SEM images of (a, b) $Co(PhPO_3)$ and (c) $Co_2P_2O_7$-900.

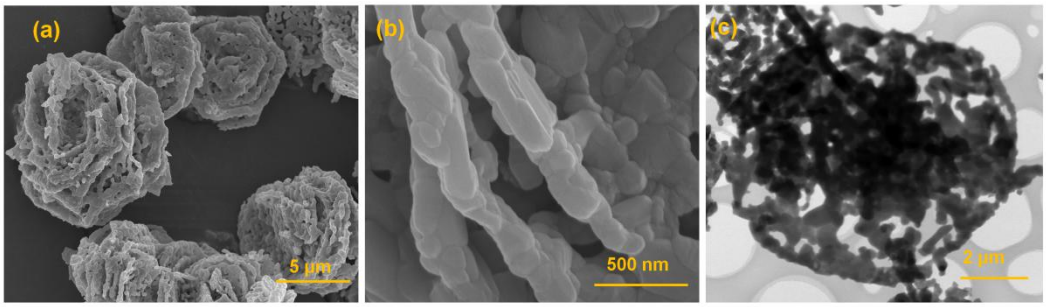

Figure S4. The SEM images (a, b) and TEM image (c) of $Co_2P_2O_7$/C-900.

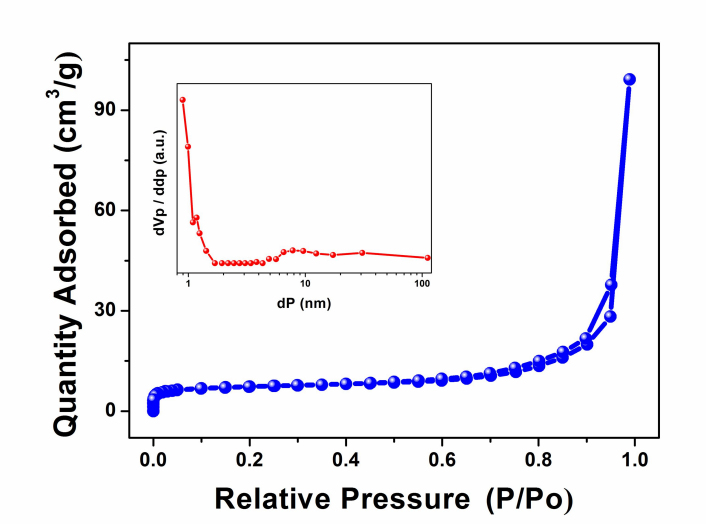

Figure S5. The N_2 adsorption and desorption isotherms and pore size distribution curve of $Co_2P_2O_7$/C-900.

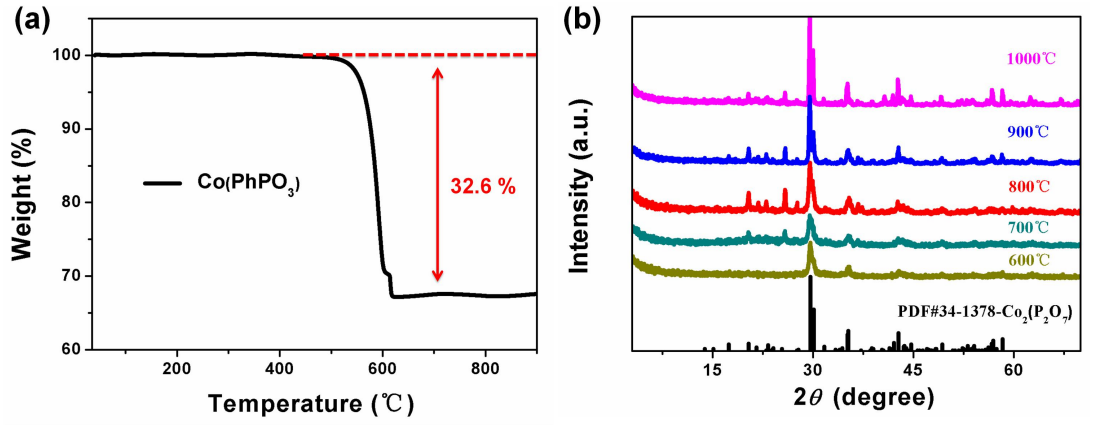

Figure S6. (a) The Thermogravimetric analysis of $Co(PhPO_3)$ precursor. (b) The PXRD patterns of $Co_2P_2O_7$/C-600, $Co_2P_2O_7$/C-700, $Co_2P_2O_7$/C-800, $Co_2P_2O_7$/C-900 and $Co_2P_2O_7$/C-1000.

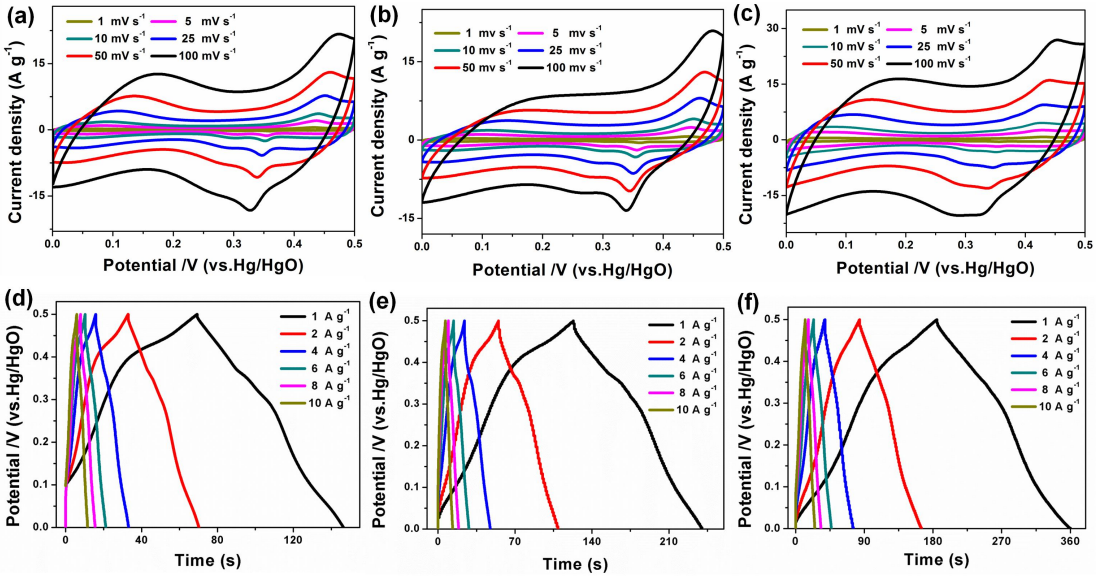

Figure S7. The CV curves (a), (b), (c) and GCD curves (d),(e), (f) of the $Co(PhPO_3)$, $Co_2P_2O_7$-900 and $Co_2P_2O_7$/C-900.

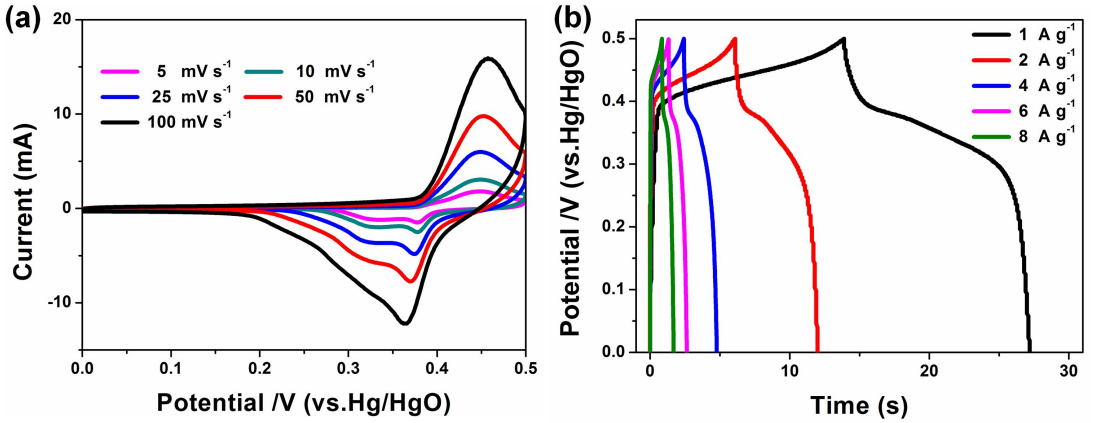

Figure S8. The electrochemical performance of Ni foam: (a) the CV curves (b) the GCD curves.

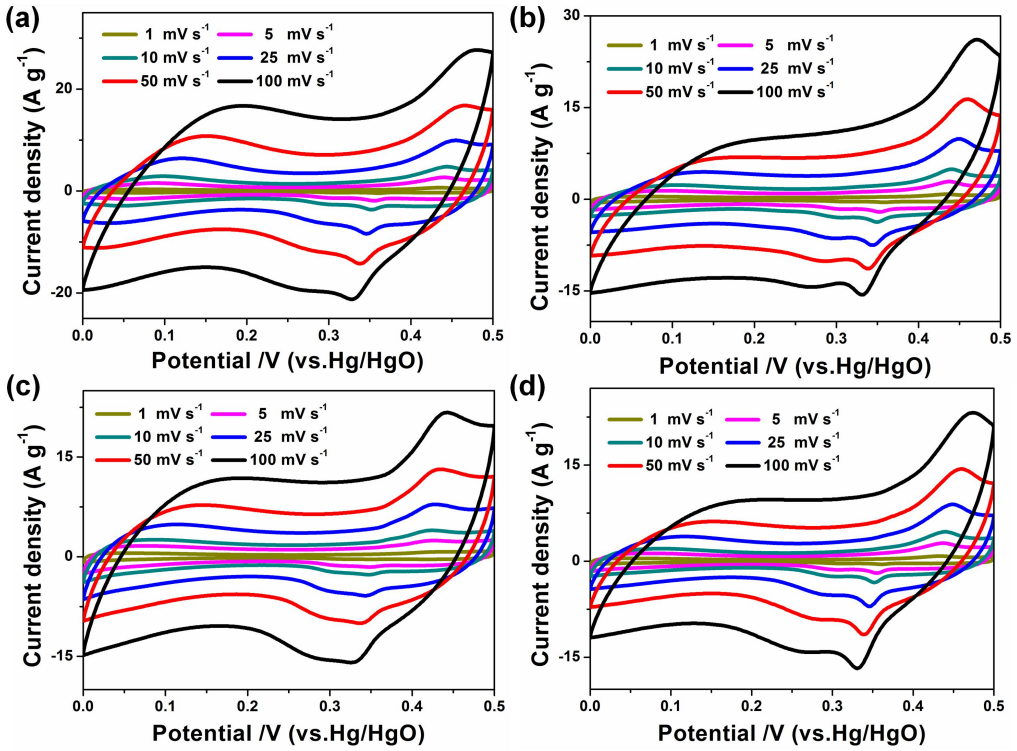

Figure S9. The CV curves of the $Co_2P_2O_7$/C-600 (a), -700 (b), -800 (c) and -1000 (d) within the potential of 0-0.5 V (vs. Hg/HgO) at various scan rates.

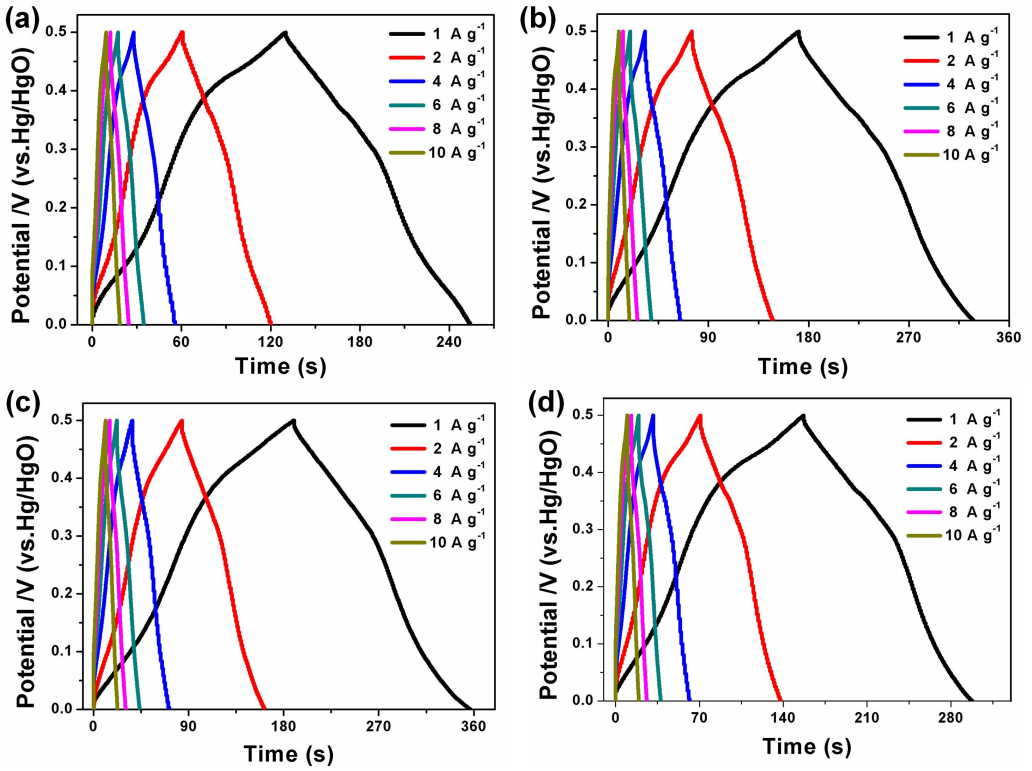

Figure S10. The GCD curves of the $Co_2P_2O_7$/C-600 (a), -700 (b), -800 (c) and -1000 (d) at various current densities.

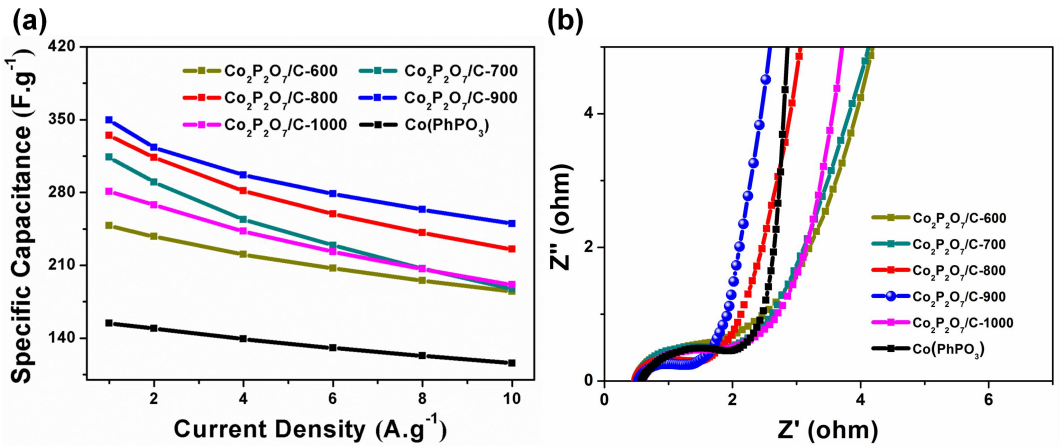

Figure S11. The specific capacitance (a) and the Nyquist plots (b) of $Co_2P_2O_7$/C-X and $Co(PhPO_3)$.

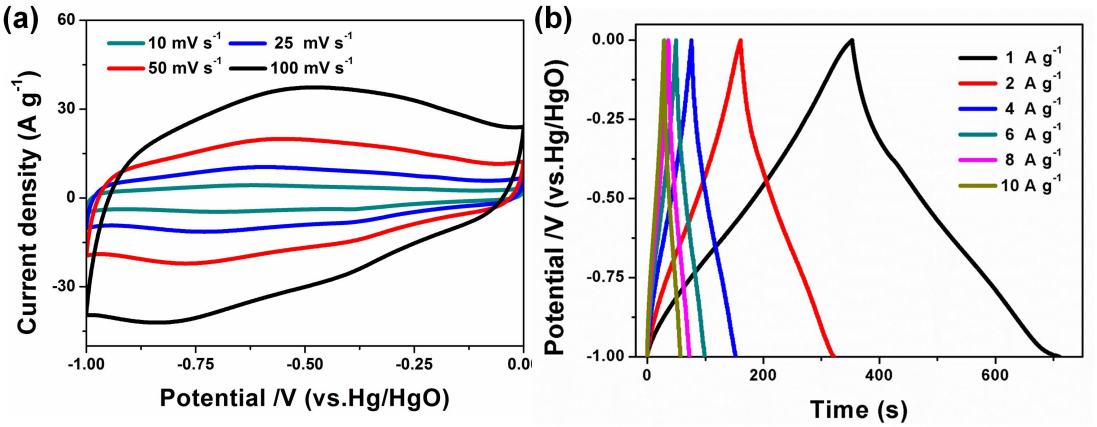

Figure S12. The CV (a) and GCD (b) curves of the 3DPG anode.

4. Equation:

$$C = \frac{I\Delta t}{m\Delta V} \qquad \text{(S1)}$$

Where C is the specific capacitance, I (A) is the discharge current, Δt (s) is the discharging time, m (g) is the mass of the active material, and ΔV (V) is the potential range

$$i = k_1 v^{1/2} + k_2 v \qquad \text{(S2)}$$

Where i and v stand for the peak current density and scan rate, respectively. Generally, $k_1 v^{1/2}$ and $k_2 v$ are associated with the bulk process contribution and the surface process contribution of the peak current density, respectively.

$$C^- \Delta V^- m^- = C^+ \Delta V^+ m^+ \qquad \text{(S3)}$$

Where C^-, ΔV^- and m^- are the specific capacity, working potential range and mass of the 3DPG electrode material, respectively. The C^+, ΔV^+ and m^+ are the the specific capacity, working potential range and mass of the $Co_2P_2O_7$/C-900 electrode material, respectively.

$$E = \frac{0.5 \times C \times \Delta V^2}{3.6} \qquad \text{(S4)}$$

Where E is the energy density (Wh kg^{-1}), C is the specific capacitance, and ΔV (V) is the potential range .

$$P = \frac{E}{\Delta t} \qquad \text{(S5)}$$

Where P is the powerty density (kW kg^{-1}), E is the energy density (Wh kg^{-1}), Δt (s) is the discharging time.

Table S1. Parameters of the proposed equivalent circuit model.

Element Samples	Rs (Ω)	Rct (Ω)	CPE-T (F)	CPE-P	W-R (Ohm)	W-T	W-P
$Co_2P_2O_7$/C-600	0.485	0.879	0.019	0.704	2.495	1.193	0.458
$Co_2P_2O_7$/C-700	0.460	0.712	0.006	0.869	4.555	1.879	0.428
$Co_2P_2O_7$/C-800	0.466	0.687	0.006	0.834	2.728	1.426	0.438
$Co_2P_2O_7$/C-900	0.518	0.578	0.010	0.779	1.973	1.099	0.445
$Co_2P_2O_7$-900	0.440	0.738	0.010	0.816	8.332	2.858	0.451
$Co_2P_2O_7$/C-1000	0.569	0.940	0.008	0.797	4.331	1.974	0.453
$Co(PhPO_3)$	0.566	1.062	0.013	0.750	2.353	0.691	0.469