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## **Supporting Information**

## Rapid Synthesis of Size-Tunable Transition Metal Carbide Nanodots under Ambient Condition

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**Figure S1.** Optical images of the sample during microwave treatment with the time interval labeled as two seconds.



Figure S2. The TEM image of pure GO sample.



**Figure S3.** (a-c) TEM images of Mo<sub>2</sub>C nanodots achieved by different concentrations of peroxomolybdic acid: (a) 0.3 mL, (b) 0.5 mL, (c) 0.7 mL, respectively. (d-f) TEM images of W<sub>2</sub>C nanodots achieved by different concentrations of peroxotungstic acid: (c) 0.3 mL, (d) 0.5 mL, and (e) 0.7 mL, respectively.







Figure S5. (a) TEM images of  $Mo_2C$  achieved by 1 mL peroxomolybdic acid after 120 s microwave treatment. (b) TEM images of  $W_2C$  nanodots achieved by 1 mL peroxotungstic acid after 90 s microwave treatment.



**Figure S6.** (a) TEM images of WC nanodots achieved by 0.3 mL peroxotungstic acid after 120 s microwave time. (b) XRD pattern of the as-synthesized WC nanodots.



**Figure S7.** The XRD patterns of the hybrid composites fabricated by precursors of phosphomolybdic acid and phosphotungstic acid after microwave treatment for 120 s and 90 s, respectively.



**Figure S8.** (a) The XPS survey spectra and (b) High-resolution XPS spectra of C 1s for P-Mo<sub>2</sub>C-5 sample.



Figure S9. (a) The XPS survey spectra and (b) High-resolution XPS spectra of C 1s

for P-W<sub>2</sub>C-3 sample.



Figure S10. (a) Polarization curves and (b) Tafel plots of 20% Pt /C,  $W_2C-4$ ,  $W_2C-10$ ,  $W_2C-24$ ,  $Mo_2C-6$ ,  $Mo_2C-14$  and  $Mo_2C-31$  samples in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (c) Polarization curves and (d) Tafel plots of 20% Pt /C,  $W_2C-4$ ,  $W_2C-10$ ,  $W_2C-24$ ,  $Mo_2C-6$ ,  $Mo_2C-14$  and  $Mo_2C-31$  samples in 0.1 M KOH.



Figure S11. Polarization curves of 20% Pt /C, pure GO, P-doped GO, P-W<sub>2</sub>C-3 and P-Mo<sub>2</sub>C-5 samples in  $0.5 \text{ M H}_2\text{SO}_4$ .

Peak	Position BE (eV)	Atomic Conc %	Mass Conc %
O 1s	530.700	7.20	4.85
C 1s	284.550	82.25	21.63
Р 2р	132.200	1.26	1.64
Mo 3d	230.050	9.29	71.88

**Table S1.** The ratios of O, C, P, Mo elements of XPS in phosphorus doped Mo<sub>2</sub>C and graphene composites.

Peak	Position BE (eV)	Atomic Conc %	Mass Conc %
O 1s	530.550	8.27	6.09
C 1s	284.400	80.53	5.05
Р 2р	133.000	0.84	1.20
W 4f	33.100	10.36	87.66

**Table S2.** The ratios of O, C, P, W elements of XPS in phosphorus doped W<sub>2</sub>C and graphene composites.



**Figure S12.** The long-term durability tests of P-W<sub>2</sub>C-3 sample at  $\eta$ =60 mV.



**Figure S13.** The XRD patterns of P-W<sub>2</sub>C-3 and P-Mo<sub>2</sub>C-5 before and after stability test in acid media.



**Figure S14.** (a) TEM image of the P-Mo<sub>2</sub>C-5 sample after HER in 0.5 M  $H_2SO_4$ . (b) TEM image of the P-W<sub>2</sub>C-3 sample after stability test in 0.5 M  $H_2SO_4$ .