Electronic Supplimentary Information

General Synthesis of Nanostructured Phase-pure Bimetallic Carbides of Molybdenum and Tungsten

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1. Experimental detail

Synthesis of Mo_2C via Carbothermal Hydrogen Reduction

Activated carbon (AC) was impregnated in a rotary evaporator at room temperature with an aqueous solution of ammonium heptamolybdate or an aqueous solution of ammonium heptamolybdate and nickel nitrate mixture. The molybdenum content was 20 wt. %. And Ni/Mo molar ratio was 0.1. After evaporating and drying in air at 80 °C overnight, the resulting mixture (0.5 g) was transferred to a quartz boat placed in a quartz tube reactor. After expelling air by argon at room temperature for 1 h, the temperature was increased linearly to the target temperature at 5 °C/min under a flow of H_2 (60 mL/min) and hold for 1 h. After cooled naturally to room temperature, the gas was switched off to allow the slow diffusion of air back into the tube to passivate the carbide surface to avoid bulk oxidation.

Hydrothermal Synthesis of Bimetallic Oxides

$CoMoO_4$: All solvents and reagents were used as received. In a typical synthesis of bimetallic oxide using hydrothermal method, the process for

preparing nickel molybdenum oxide is selected as the representative. 0.005 mol of $Na_2MoO_4 \cdot 2H_2O$ and 0.005 mol of $Co(NO_3)_2 \cdot 6H_2O$ were respectively dissolved in 20 mL of deionized water and combined at room temperature with stirring. After stirring for 30 min, the mixture was transferred and sealed in a 60 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 180 °C for 4 h. Then the autoclave was taken out of the oven and cool to room temperature naturally. The precipitate was harvested via centrifugation, washed thoroughly with water and ethanol, and dried at 80 °C overnight. Finally the product was ground to a fine powder for characterization.

$FeMoO_4$: All solvents and reagents were used as received. In a typical synthesis of bimetallic oxide using hydrothermal method, the process for preparing nickel molybdenum oxide is selected as the representative. 0.005 mol of $Na_2MoO_4 \cdot 2H_2O$ and 0.005 mol of $Fe(NO_3)_2 \cdot 6H_2O$ were respectively dissolved in 20 mL of deionized water and combined at room temperature with stirring. After stirring for 30 min, the mixture was transferred and sealed in a 60 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 180 °C for 4 h. Then the autoclave was taken out of the oven and cool to room temperature naturally. The precipitate was harvested via centrifugation, washed thoroughly with water and ethanol, and dried at 80 °C overnight. Finally the product was ground to a fine powder for characterization.

$CoWoO_4$: All solvents and reagents were used as received. In a typical synthesis of bimetallic oxide using hydrothermal method, the process for preparing nickel molybdenum oxide is selected as the representative. 0.005 mol of $Na_2WO_4 \cdot 2H_2O$ and 0.005 mol of $Co(NO_3)_2 \cdot 6H_2O$ were respectively dissolved in 20 mL of deionized water and combined at room temperature with stirring. After stirring for 30 min, the mixture was transferred and sealed in a 60mL Teflon-lined stainless steel autoclave and kept in an electric oven at 180 °C for 4 h. Then the autoclave was taken out of the oven and cool to room temperature naturally. The precipitate was harvested via centrifugation, washed thoroughly

with water and ethanol, and dried at 80 °C overnight. Finally the product was ground to a fine powder for characterization.

$NiWoO_4$: All solvents and reagents were used as received. In a typical synthesis of bimetallic oxide using hydrothermal method, the process for preparing nickel molybdenum oxide is selected as the representative. 0.005 mol of $Na_2WO_4·2H_2O$ and 0.005 mol of $Ni(NO_3)_2·6H_2O$ were respectively dissolved in 20 mL of deionized water and combined at room temperature with stirring. After stirring for 30 min, the mixture was transferred and sealed in a 60 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 180 °C for 4 h. Then the autoclave was taken out of the oven and cool to room temperature naturally. The precipitate was harvested via centrifugation, washed thoroughly with water and ethanol, and dried at 80 °C overnight. Finally the product was ground to a fine powder for characterization.

*$FeWoO_4$***:** All solvents and reagents were used as received. In a typical synthesis of bimetallic oxide using hydrothermal method, the process for preparing nickel molybdenum oxide is selected as the representative. 0.005 mol of $Na_2WO_4·2H_2O$ and 0.005 mol of $Fe(NO_3)_2·6H_2O$ were respectively dissolved in 20 mL of deionized water and combined at room temperature with stirring. After stirring for 30 min, the mixture was transferred and sealed in a 60 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 180 °C for 4 h. Then the autoclave was taken out of the oven and cool to room temperature naturally. The precipitate was harvested via centrifugation, washed thoroughly with water and ethanol, and dried at 80 °C overnight. Finally the product was ground to a fine powder for characterization.

2. Figures and Table

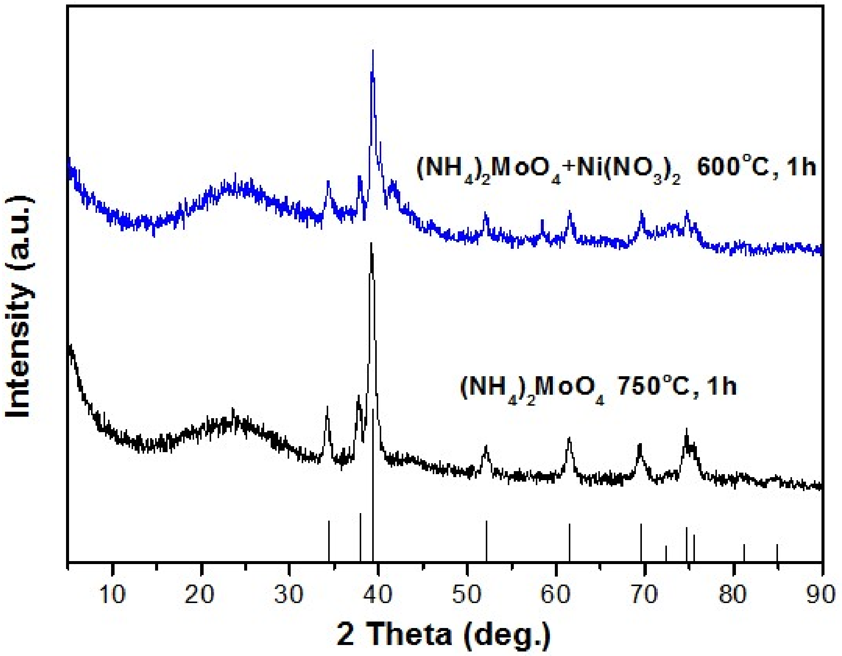


Figure S1. XRD patterns of the products obtained by carbothermal hydrogen reduction of $(NH_4)_2MoO_4$ at 750 °C and $(NH_4)_2MoO_4$+$Ni(NO_3)_2$ at 600°C for 1 h. The standard pattern of Mo_2C (PDF#35-0787) is shown (solid lines) at the bottom.

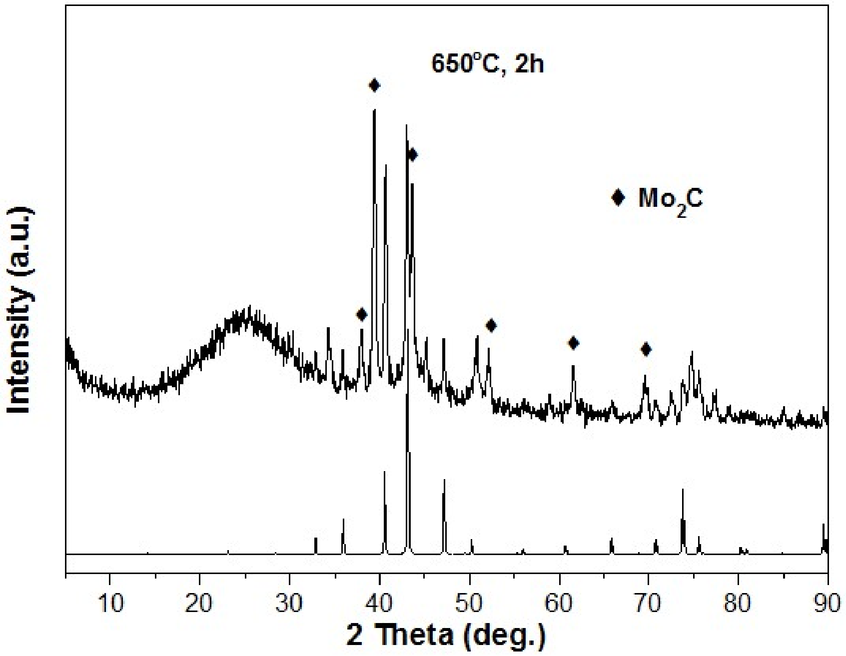


Figure S2. XRD patterns of the products obtained by carbothermal hydrogen reduction of $NiMoO_4$ without hydrothermal treatment at 650 °C for 2 h. The simulated pattern of Ni_6Mo_6C (PDF#80-0337) is shown (solid lines) at the bottom.

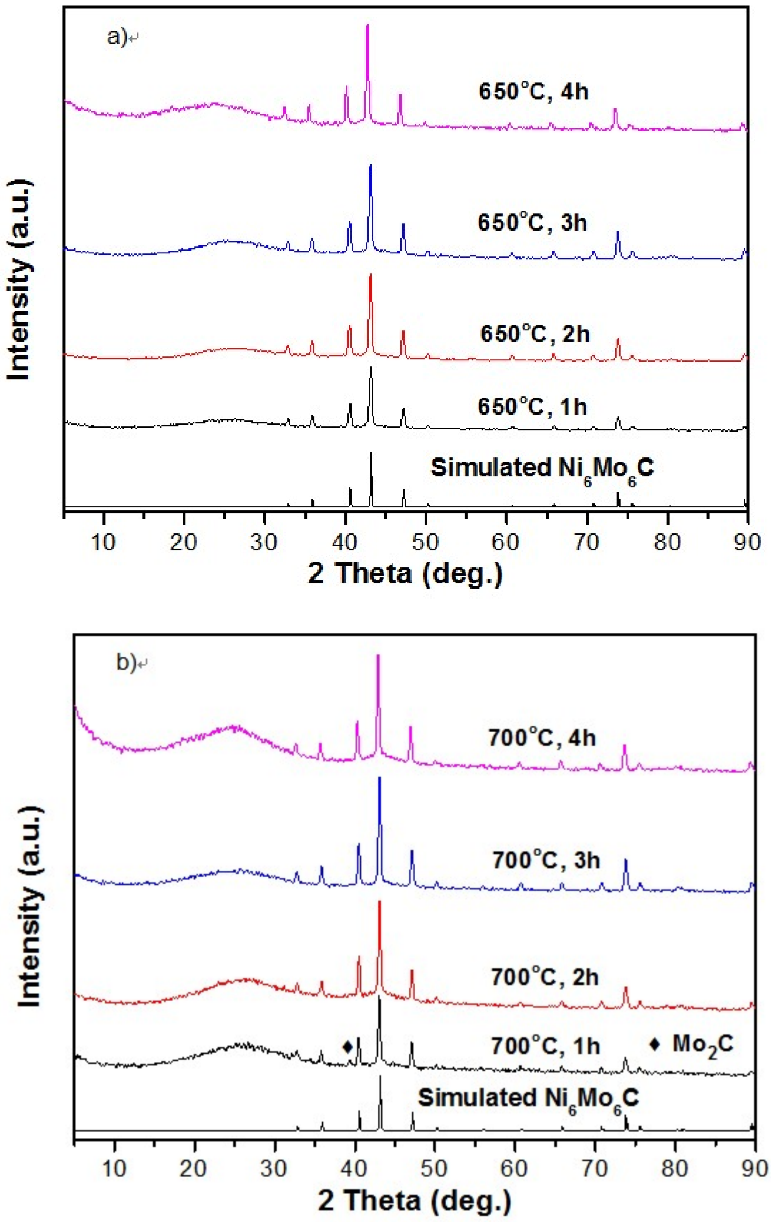


Figure S3. XRD patterns of the products obtained by carbothermal hydrogen reduction of $NiMoO_4 \cdot nH_2O$ at 650 °C (a) and 700°C (b) for 1-4 h.

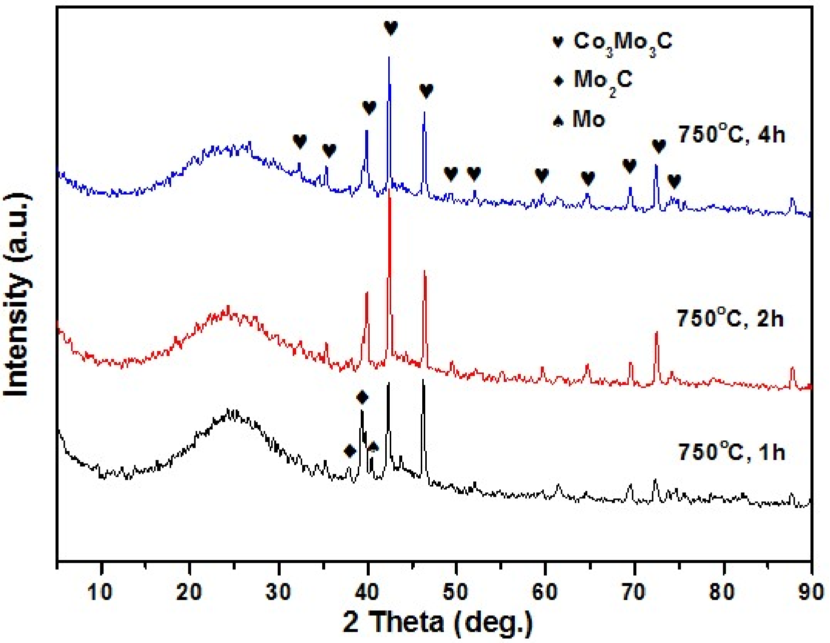
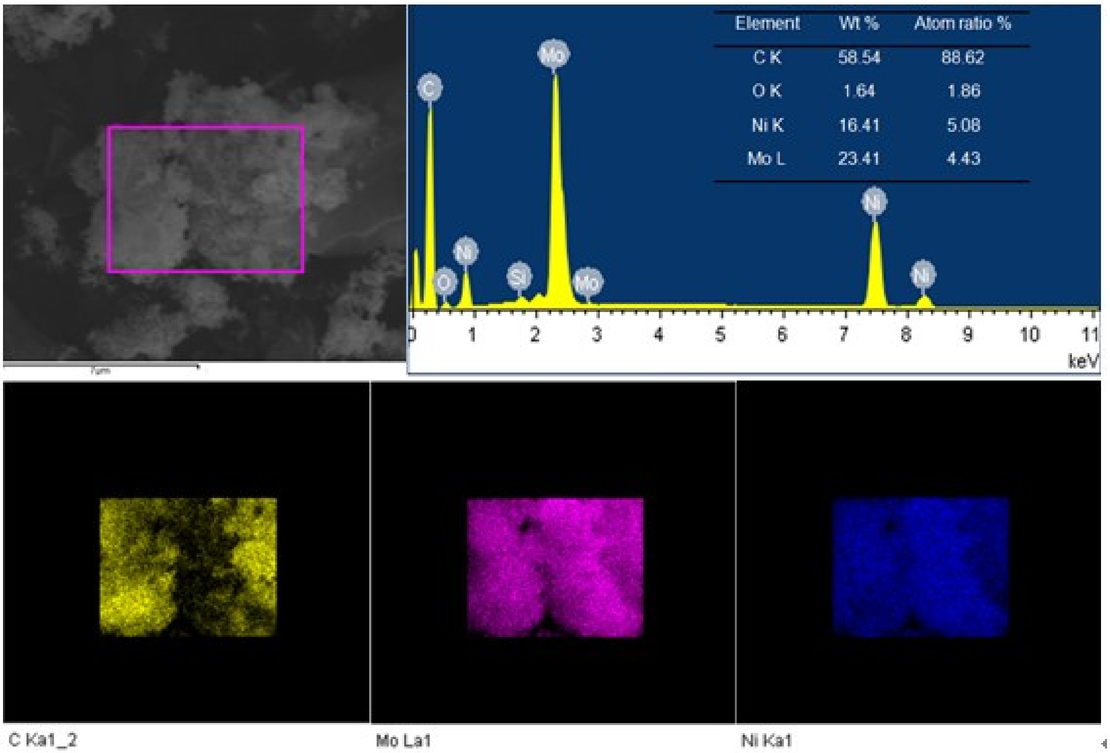


Figure S4. XRD patterns of the products obtained by carbothermal hydrogen reduction of $CoMoO_4 \cdot nH_2O$ at 750 °C for 1-4 h.



Element	Wt %	Atom ratio %
C K	58.54	88.62
O K	1.64	1.86
Ni K	16.41	5.08
Mo L	23.41	4.43

Figure S5.SEM energy dispersive spectroscopy and elemental mapping images of Ni_6Mo_6C.

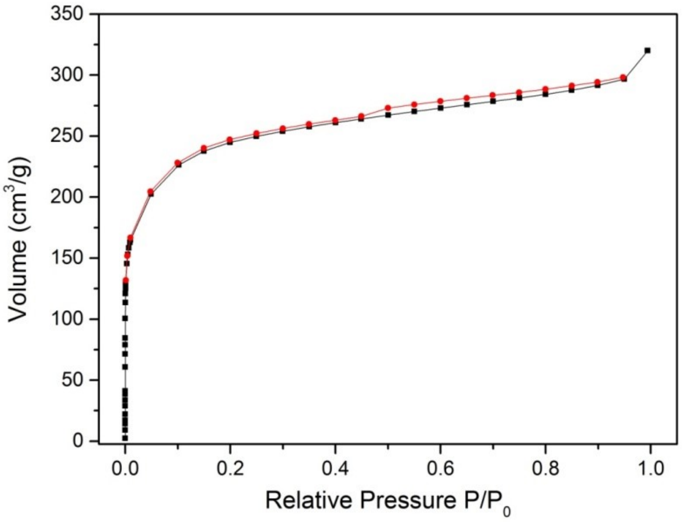


Figure S6. N_2 sorption isotherms of Ni_6Mo_6C obtained at 650 ^oC for 4 h.

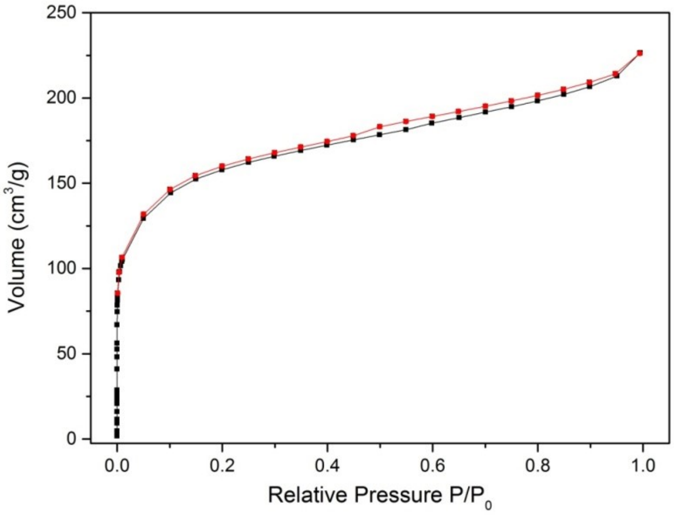


Figure S7. N_2 sorption isotherms of Fe_3Mo_3C obtained at 800 °C for 4 h.

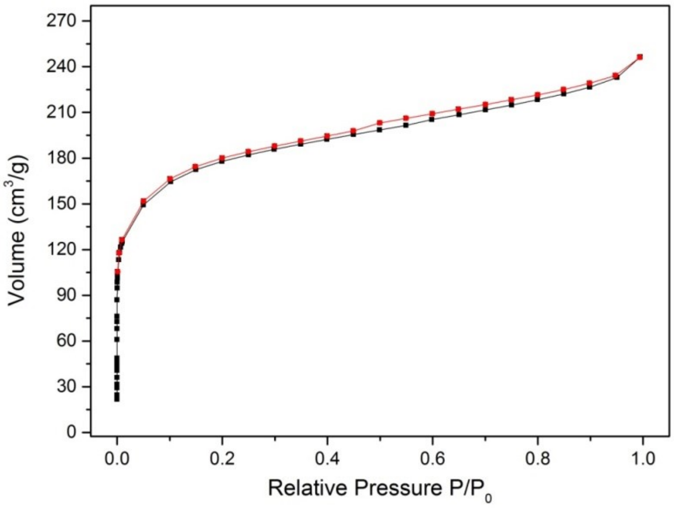


Figure S8. N_2 sorption isotherms of Co_6W_6C obtained at 800 °C for 4 h.

Table S1. Carbon contents, specific surface area, total pore volume, and average pore radius of the bimetallic carbide samples

Sample	C content[a] (wt%)	Total Pore Volume[b] (cm^3/g)	Average Pore Radius[b] (nm)	S_{BET}[b] (m^2/g)
Ni_6Mo_6C (650 °C for 4 h)	60	0.495	1.1	868
Fe_3Mo_3C (800 °C for 4 h)	39	0.350	1.3	553
Co_6W_6C (800 °C for 4 h)	33	0.342	1.3	523

[a]Determined by CHN analysis. [b] Specific surface area, total pore volume and average pore radius were calculated by the Brunauer −Emmett −Teller method and BJH method.

Scheme S1. Reaction pathways for the hydrogenation of naphthalene.