Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

for

Crystal Structure and Morphology Control of Molybdenum Carbide Nanomaterials Synthesized from an Amine-metal Oxide Composite

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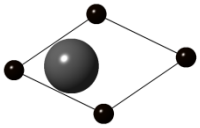
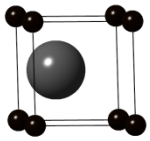
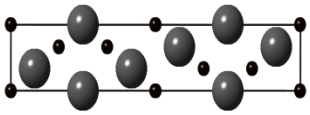
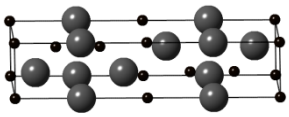
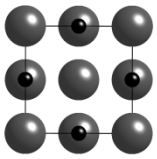
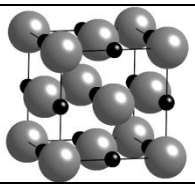
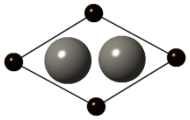
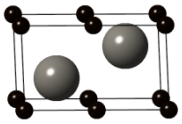
1. Synthesis method:

All chemicals were purchased from Sigma-Aldrich, Mallinckrodt, and Certified Reagent chemicals. The amine-metal oxide composite was made by mixing Ammonium heptamolybdate and amines in water, then adjusting the pH<3. In this method, amines are regarded as the carbon sources, the reducing agents, and the structure directing agents. 1.00g (0.81mmol) Ammonium heptamolybdate and 2.45g (22.66mmol) p-phenylendiamine (amine:Mo=4:1) were dissolved into 50ml water. Hydrochloric acid was used to adjust the pH value to lower than 3, which causes the precipitate to form. The solution was further heated to 50^{o}C while stirring for ~2.5h. The precipitate was collected by centrifuged and washed with water and ethanol. After each washing, the system was centrifuged at 5500 RPM for 10min. The solution was finally decanted and the wet precipitate was placed in the drying oven at 50^{o}C for 24h. The amine-metal oxide composites were calcined to form metals carbides in a tube furnace in the present of Argon. The ramping rate in tube furnace was controlled at 1.67^{o}C/min and the samples were naturally cooled down to room temperature in the tube furnace.

2. Characterization

The X-ray diffraction patterns (XRD) were measured on a Bruker-AXS Smart Apex II CCD diffractmeter, which is equipped with an Oxford Cobra Cryosystem and employs Mo-Kα source (λ=0.70926Å). The data contained in the PDF2 database was used to analyze the XRD experiment results. The distance between sample and the detector is kept at 61.3mm. Scanning electron microscope (SEM) images were captured on an FEI QUANTA 450 with Shottky Field Emitter Gun. Both secondary electron and backscattering electron signal were taken using a 20kV accelerating energy. The High Resolution Transmission Electron Microscopy (HRTEM) images were recorded on an FEI Tecnai G2 F20 200 kV (S) TEM. The TEM samples were prepared by ultrasonicating ~20mg samples in 5ml ethanol for 15min on the 3510 Branson Bath Sonicator. After sonicating, 100µl of above solution was dropped onto Formvar Film 400 Square Mesh, Copper Grids.

Table S1 Crystal name and corresponding structures for four types of molybdenum carbids

Name	Structure	
γ-MoC (WC type)		
ŋ-MoC (MoC type)		
α-MoC_{1-x} (NaCl type)		
β-Mo_2C (Fe_2N type)		

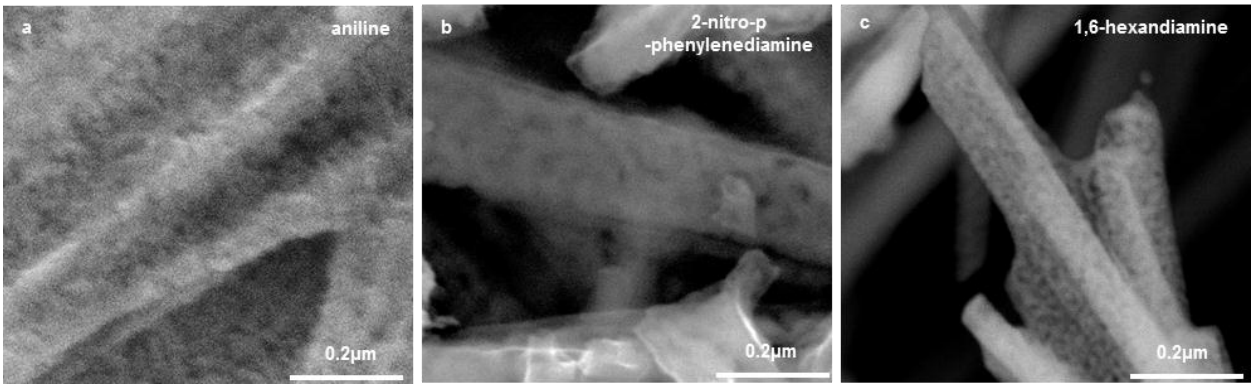


Figure S1. High resolution SEM images of porous β-Mo_2C nano-particles synthesized by (a) aniline, at 675°C, (b) 2-nitro-*p*-phenylenediamine, at 875°C, (c) 1,6-hexanediamine, at 675°C.

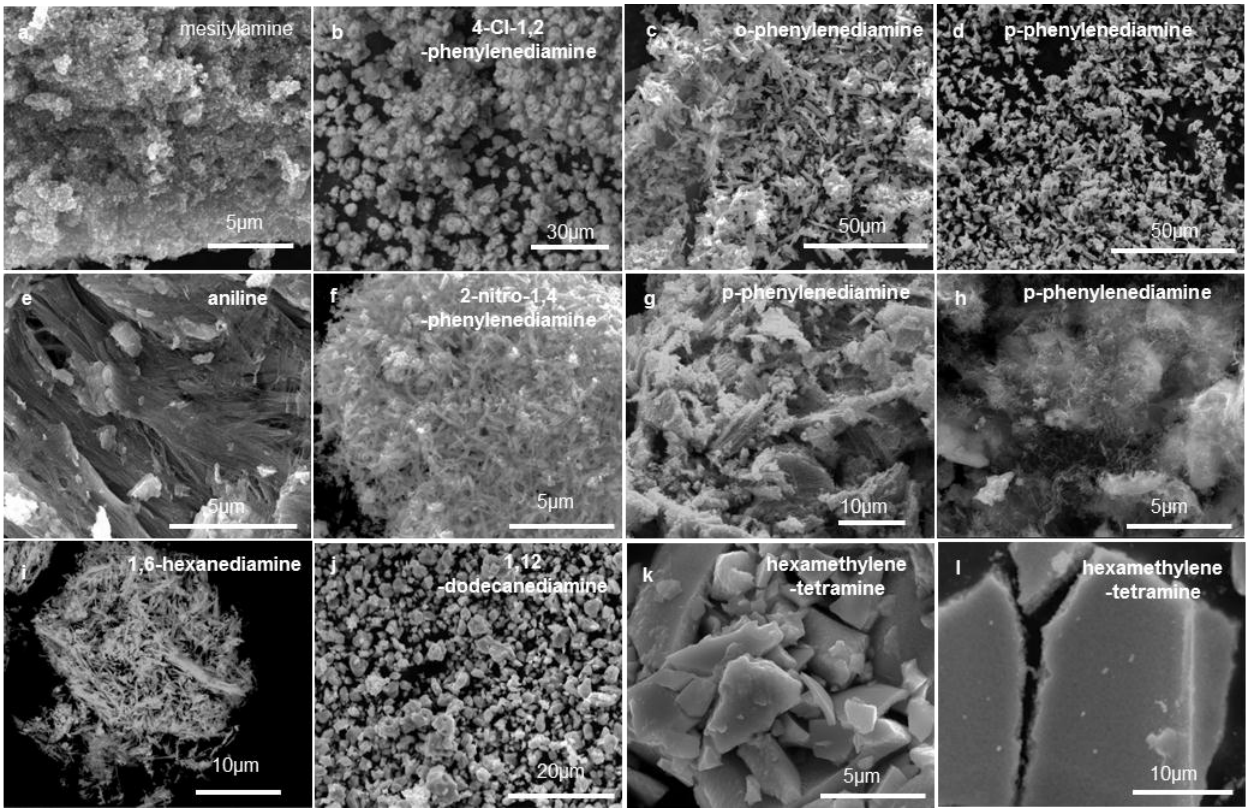


Figure S2. The coresponding large area SEM images of, (a) β-Mo_2C synthesized by mesitylamine, at 750°C (b) β-Mo_2C synthesized by 4-Cl-*o*-phenylenediamine, 675°C (c) α-MoC_{1-x} synthesized by *o*-phenylenediamine, at 625°C (d) α-MoC_{1-x} synthesized by *p*-phenylenediamine, at 675°C (e) β-Mo_2C synthesized by aniline, at 675°C (f) β-Mo_2C synthesized by 2-nitro-*p*-phenylenediamine, at 875°C, (g) α-MoC_{1-x} synthesized by *p*-phenylenediamine, at 675°C, and amine: Mo=4:1, (h) α-MoC_{1-x} synthesized by *p*-phenylenediamine, at 850°C, and amine: Mo=8:1, (i) β-Mo_2C synthesized by 1,6-hexanediamine, at 675°C, (j) α-MoC_{1-x} synthesized1,12-dodecanediamine, at 675^{o}C (k) α-MoC_{1-x} synthesized by hexamethylenetetramine, at 850^{o}C, (l) β-Mo_2C synthesized by hexamethylenetetramine, at 900^{o}C. In addition to (g) and (h), the molar ratio of amine: Mo=2:1

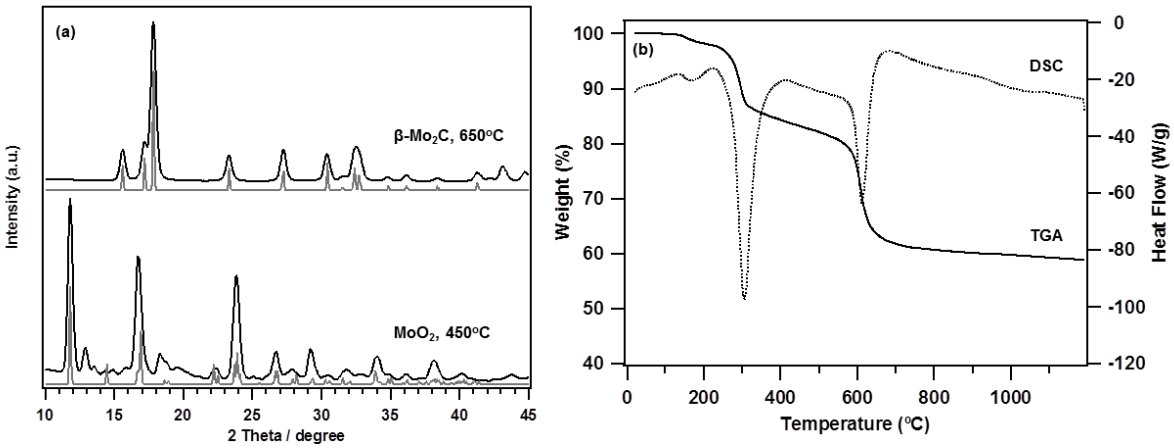


Figure S3. (a) XRD patterns of the post-calcined sample at 450^{o}C and at 650^{o}C, at the *o*-phenylendiamine: Mo=2:1, (b) TGA/DSC curves for *o*-phenylendiamine/ $(NH_4)_6Mo_7O_{24}$ system.

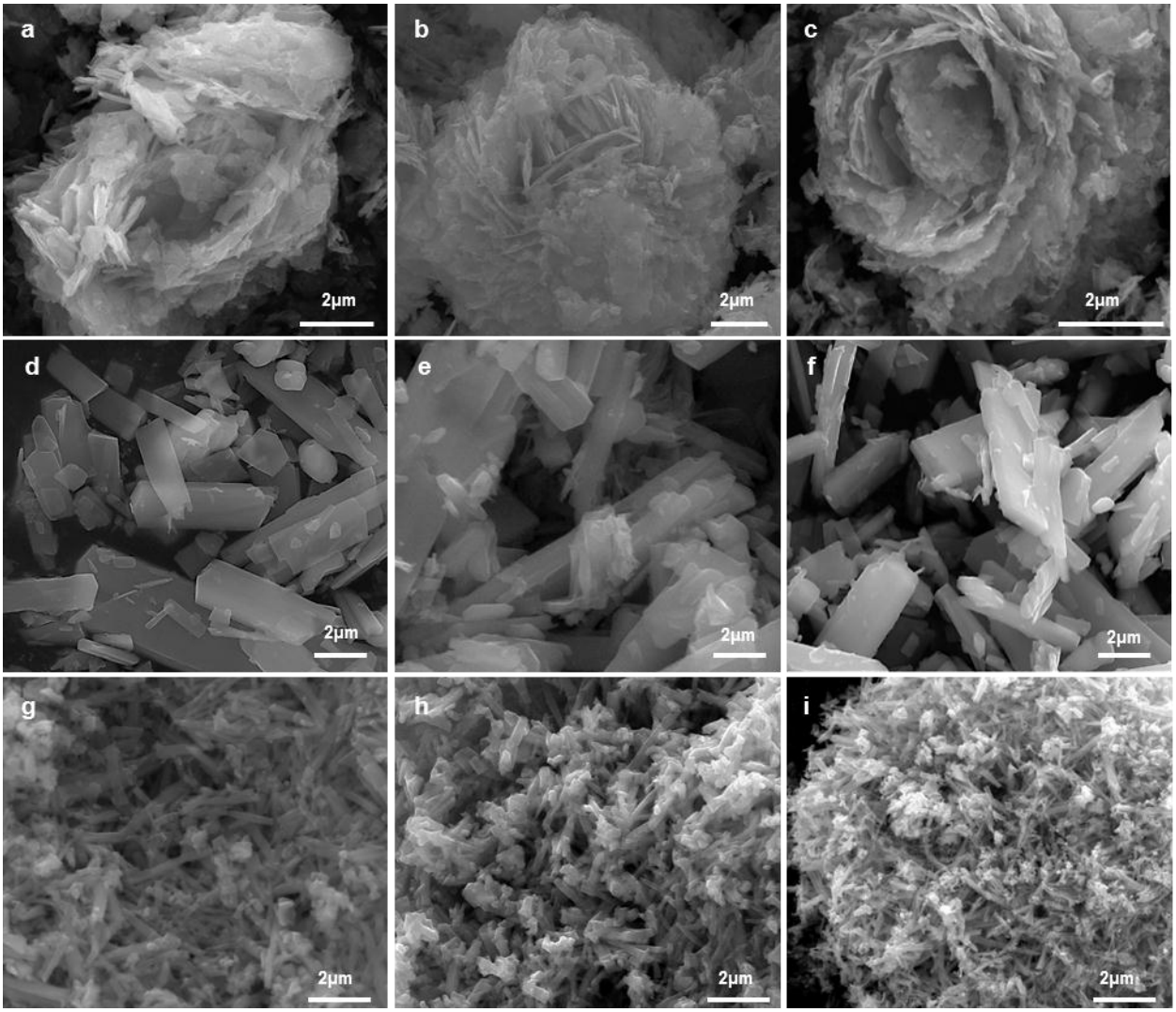


Figure S4. SEM images of the micro-flowers synthesized by 4-Cl-*o*-phenylenediamine at (a) 350°C, (b) 450°C, and (c) 675°C, the flake-like particles synthesized by *o*-phenylenediamine at (d) 350°C, (e) 450°C, and (f) 625°C, and the nano-rods synthesized by 2-nitro-*p*-phenylenediamine at (g) 350°C, (h) 450°C, and (i) 875°C. The molar ratio of amine: Mo=2:1.

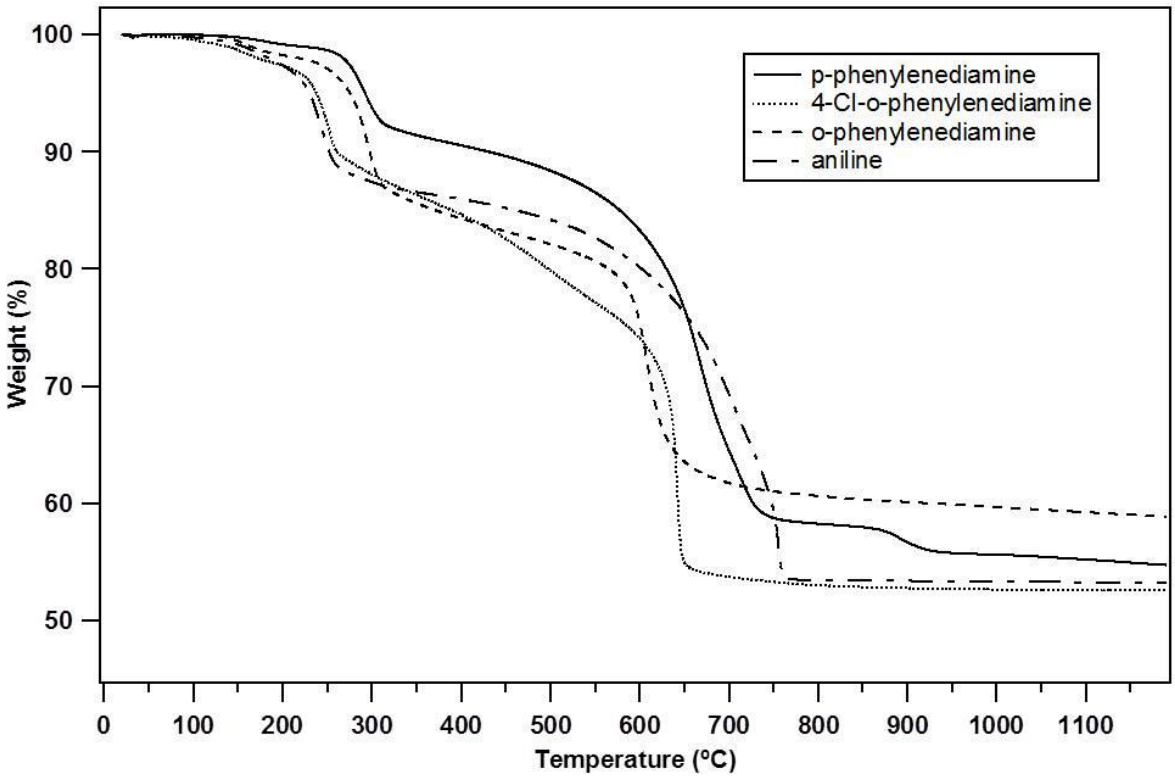


Figure S5. TGA curves for (a) *o*-phenylendiamine/$(NH4)_6Mo_7O_{24}$ system, (b) *p*-phenylendiamine/$(NH_4)_6Mo_7O_{24}$ system, (c) aniline/$(NH_4)_6Mo_7O_{24}$ system, (d) 4-Cl-*o*-phenylendiamine/$(NH_4)_6Mo_7O_{24}$ system, at amine: Mo=2:1