Electronic Supplementary Information

Direct access to macroporous chromium nitride and chromium titanium nitride with inverse opal structure

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Experimental procedures

Synthesis

All chemicals were purchased and used without further purification. Polystyrene (PS) beads were used as template and metal chloride complexes were used as metal precursors in the synthesis of macroporous CrN. Carboxylate-functionalized Polystyrene (PS) beads (500-nm-radius) in a 2.7 vol. % aqueous suspension was mixed with ethylene glycol and water in a ratio of 1: 0.4: 6. The mixed solution was sonicated for 10 minutes before dropping on a polystyrene Petri dish followed by drying on a hot plate at 50°C for 48 hours. The solution was completely dry after this process. The product is a white film, which is scraped off and weighed. 0.0343g CrCl₃·6H₂O was completely dissolved in 10 mL of ethanol and was mixed with 0.0200g of the scraped polystyrene. For the synthesis of chromium titanium nitride, half the amount of the chromium precursor was used, with the addition of equivalent amount (molar ratio) of TiCl₄·2THF. The mixture was dried in a glass Petri dish on top of a hot plate of 50°C for 12 h. Then the dried product is scraped and put into an alumina boat for annealing. The boat is placed in a silica tube with airtight, stainless steel end-caps with valves on input and output gas lines. All gases were purified to remove oxygen or water using pellets of copper, nickel, palladium and platinum on zeolite supports. The silica tube was placed in a split tube furnace for annealing. The chromium precursor infiltrated PS array was heated under flowing ammonia to 450°C using a ramp rate of 50°C/hour. The product was kept at 450°C for 6 hours before a controlled cooling (100°C/h) to room temperature. For the chromium titanium sample, the infiltrated PS array was heated to 450°C and kept for 3 h before raising the temperature to 550°C. The product was held at 550°C for 24 h and then cooled. Same heating and cooling rates as for the CrN sample were used. The product is denoted as Cr_{0.5}Ti_{0.5}N. Due to the tendency to form a surface oxide upon exposure to air, all samples were carefully handled and let slowly exposed to air after annealing to minimize the extent of oxide formation.

Two samples of $Cr_{0.5}Ti_{0.5}N$, without PS templates, were made using different annealing temperature to investigate the oxygen content in the samples. The first sample, denoted as $Cr_{0.5}Ti_{0.5}N$ (550°C), was made using same method as described above except the use of PS templates and heated under ammonia for 24 h in 550°C. Using the same precursors, the second sample, denoted as $Cr_{0.5}Ti_{0.5}N$ (800°C), was heated up to 800°C for 12 h under ammonia.

For the interconversion of CrN, the macroporous CrN made from previous synthesis was heated under flowing air to 550°C for 1 hour using a ramp rate of 300°C/hour, followed by a controlled cooling to room temperature in about 2 h. To convert the annealed sample back to the nitride, samples were divided into two groups and heated in flowing ammonia at 650°C and 700°C for 6 hours, respectively, with a ramp rate of 100°C/h and a cooling rate of 200°C/h.

For the synthesis of $Cr_{0.5}V_{0.5}N$, $CrCl_3 \cdot 6H_2O$ and $VCl_3 \cdot 3THF$ were used as precursors. The annealing temperature under ammonia is set as 500°C for 24 h.

Characterization

Ground powders were examined using a Rigaku Ultima IV powder X-ray diffractometer with Cu K radiation (K α 1, λ = 1.5406 Å and K α 2, λ = 1.5444 Å). Crystal structures of the products were confirmed using PXRD profiles from the structure database. The domain sizes of the samples were calculated using the Halder-Wagner method and the lattice parameters were calculated using the whole powder pattern fitting (WPPF) technique. Thermogravimetric analysis was carried out using a TGA Q50 from TA instruments. Macroporous CrN was heated to 550°C and kept for 90 min under flowing air, using a ramp rate of 5°C/min. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were carried out with a LEO-1550 field emission SEM (FESEM). Voltage is normally set as 5kV for imaging and 15kV for compositional EDX analysis. High Resolution Transmission Electron Microscopy (HRTEM) was performed using a Shottky-fieldemission-gun Tecnai F20 operated at 200 kV. Samples were dispersed in ethanol and were sonicated using water bath sonicator before transferring to a TEM copper grid with lacy carbon film on the top. Chemical analysis was also performed using X-ray photoelectron spectroscopy (XPS). The spectra were recorded with a Surface Science Instrument SSX-100 system. Initial survey spectrum was collected for use in qualitative analysis and higher resolution narrow scan spectra were measured to analyze the chemical states of elements. The obtained XPS spectra peaks were deconvoluted using Gaussian-Lorentzian envelopes in the provided CasaXPS software. Elemental analysis of nitrogen and oxygen content in the nitride samples were conducted by a LECO TC-600 analyzer using an inert gas fusion method. Nitrogen was detected as N₂ by thermal conductivity and oxygen was detected as CO₂ by infrared method. The apparatus was calibrated using LECO standard materials.



Fig. S1 XRD pattern of macroporous CrN after thermogravimetric analysis showing a pure Cr_2O_3 phase. The inset is the elemental composition calculated by EDX in SEM.

Element	Pos./ Binding Energy (eV)	Atomic %	Atomic %
		CrN	Cr _{0.5} Ti _{0.5} N
C 1s	258.0	27.40	18.96
O 1s	530.0	26.34	32.41
Cr 2p	575.0	21.66	11.95
Ti 2p	457.0	-	11.98
Cl 2p	198.0	1.30	-
N 1s	396.0	23.31	24.70

Table S1. Elemental composition of as-made CrN and Cr_{0.5}Ti_{0.5}N determined by XPS.

Table S2. Elemental composition determined by combustion method.

Element	Mass (mg)	Oxygen (wt. %)	Nitrogen (wt. %)
Cr Ti N (550 °C)	1.53	13.99	16.75
CI-II-N (550°C)	2.59	13.95	17.04
Cr T: N (900 °C)	2.85	1.02	22.13
CI-11-IN (800°C)	2.66	0.79	22.60



Fig. S2 TGA curve of polystyrene bead decomposed in air (black) and argon gas (red).



Fig. S3 SEM image of Cr₂O₃ produced by annealing infiltrated PS beads in air. Scale bars are 1 micron.



Fig. S4 XRD pattern of as-made macroporous $Cr_{0.5}V_{0.5}N$.



Fig. S5 SEM image of macroporous $\text{Cr}_{0.5}\text{V}_{0.5}\text{N}.$