Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

A Novel Composite Hierarchical Hollow Structure: One-Pot Synthesis and Magnetic Properties of $W_{18}O_{49}/WO_2$ Hollow Nanourchins

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Experimental details

Synthesis: The tungsten oxide hollow urchins were prepared by hydrothermal treatment using tungsten hexacarbonyl ($W(CO)_6$, Aldrich, 99.9%) as a tungsten source and absolute ethanol. Typically, 0.4 g of $W(CO)_6$ was dissolved in absolute ethanol (100 mL), to achieve a concentration of 11.36 mM, and the solution was delivered into a 200 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 200°C for 20 min–24 h with gentle magnetic stirring. After cooling to room temperature, the precipitates were collected by centrifugation at 3,000 rpm for 15 min. The products were washed with ethanol and deionized water several times, and dispersed in 20 mL ethanol.

Characterization: The as-prepared micro or nanostructures were characterized and analyzed by scanning electron microscopy (SEM, JEOL JSM-7401F), X-ray diffraction (XRD, PANalytical X´Pert diffractometer with Cu Kα radiation), Cs-corrected high-resolution transmission electron microscopy (Cs-corrected HR-TEM; JEOL JEM-2200FS), and energy dispersive X-ray spectroscopy (EDX). A superconducting quantum interference device (SQUID) magnetrometer (MPMS XL-7) was used to measure the magnetization of the products.

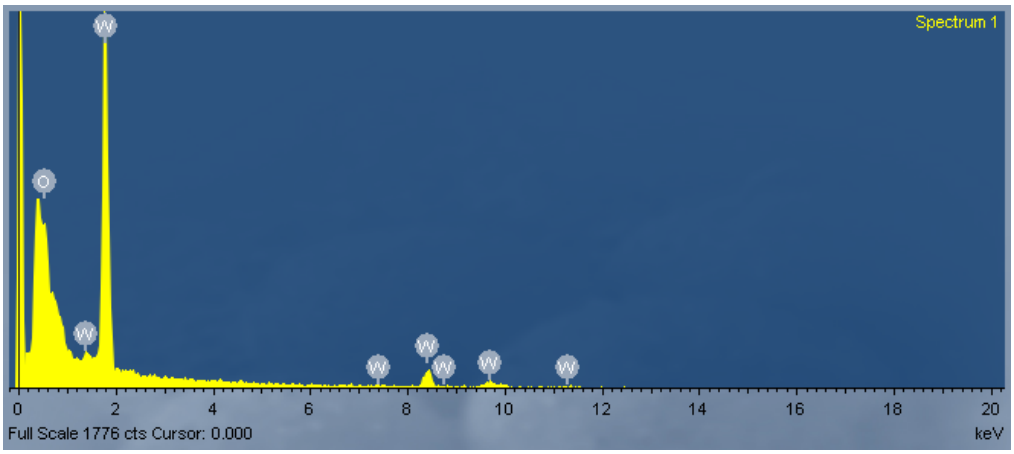

Fig. S1 Energy dispersive X-ray spectroscopy (EDS) of as-prepared products.

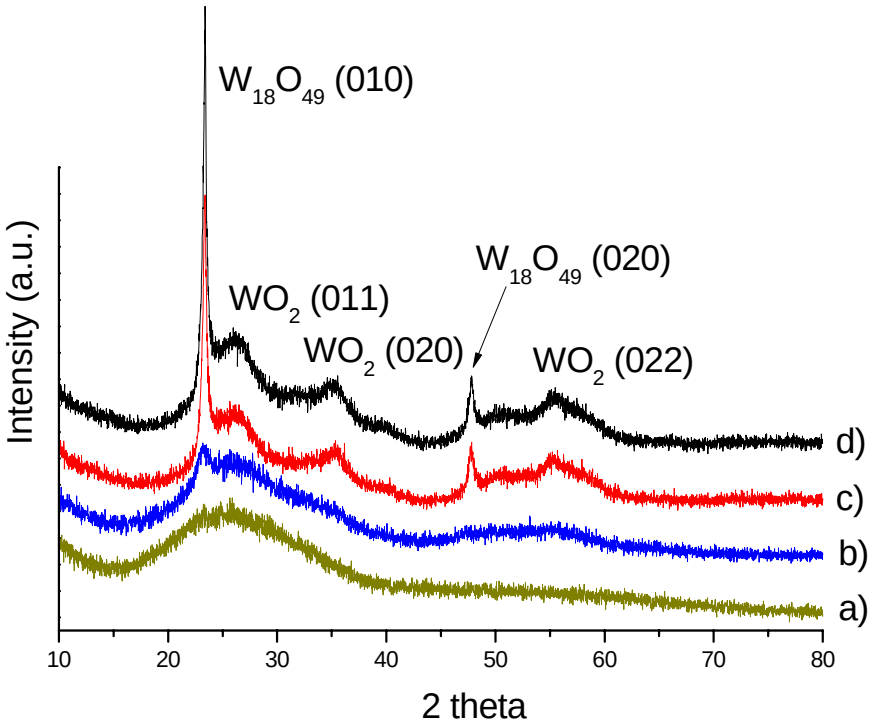

Fig. S2 XRD patterns of the intermediate products prepared with different reaction times: a) 20 min, b) 1 h, c) 12 h, d) 24 h. At early stages, smooth spherical particles were obtained (Fig. 2a), and the corresponding XRD patterns show that the initial products were amorphous WO_2 (Fig. S2a). After reaction for 1 h, small nanorods formed on the surfaces of WO_2 nanoparticles (Fig. 2b) and the weak $W_{18}O_{49}$ [010] peak appeared in XRD patterns (Fig. S2b). The nanorods on the surfaces grew longer with increasing reaction time (Fig. 2c–2e) and the intensity of $W_{18}O_{49}$ peaks were also increased accordingly (Fig. S2c-S2d). These time-

dependent SEM and XRD results indicate that the WO_2 peaks corresponds to core-spheres and the $W_{18}O_{49}$ peaks corresponds to nanorods-shell, respectively.

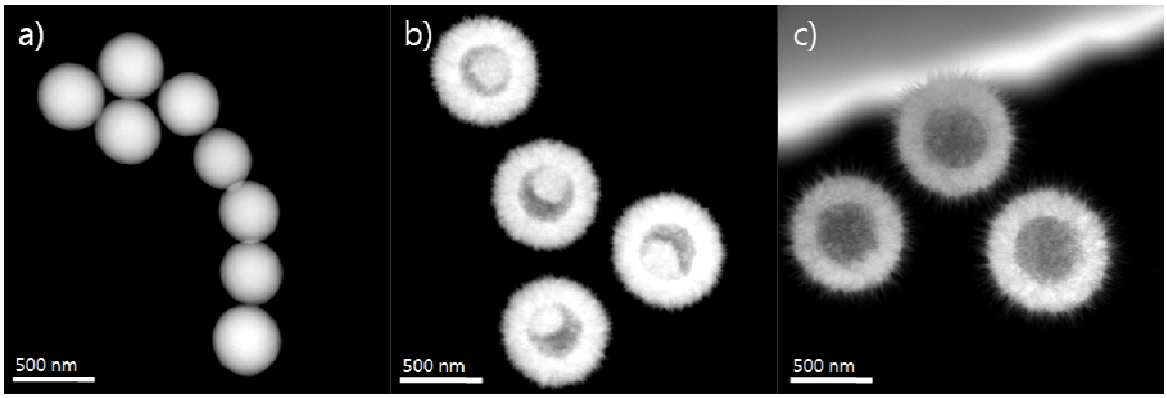

Fig. S3 Low-magnification HAADF-STEM images of the products obtained at 200°C for different reaction times: a) 20 min, b) 5 h, c) 24 h.