

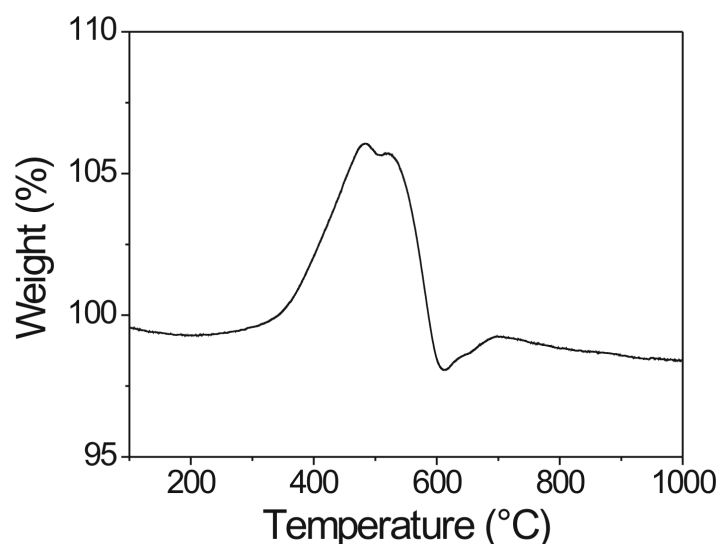


Figure S1. Thermogravimetric analysis (TGA) of hierarchical porous TiC/C. Heating the sample in oxygen to 1000 °C does not lead to significant weight loss. The reason for that can be attributed to the conversion of TiC into TiO₂ (the formation of intermediate species like TiOC cannot be excluded). On the basis of the result obtained from EDX analysis (only a miniscule amount of oxygen is present in the TiC/C composites), the carbide content was calculated to be about 75 weight percent. However, note that the carbide content can be readily adjusted by the amount of titanium isopropylate used.

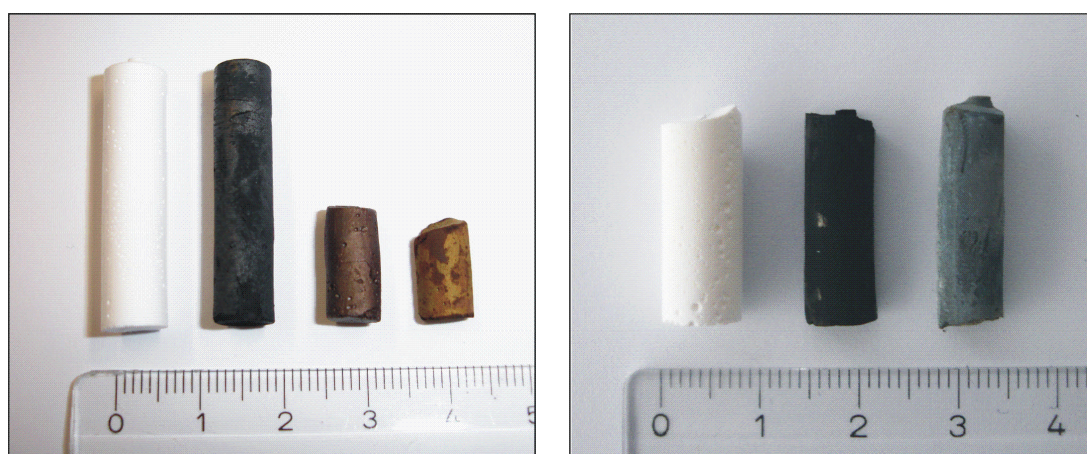


Figure S2. Photographs of different hierarchical porous monoliths. Left: from left to right: SiO₂, C, bronze-colored WC/C, brownish TiC/C. Right: from left to right: SiO₂, C, green-grayish SiC. The synthetic methods presented in this work can be used to synthesize a broad range of crack-free carbon-metal carbide monoliths with high carbide contents. Also, it is suited for the preparation of chemically pure silicon carbide with high specific surface area as shown recently [K. Sonnenburg, P.

Adelhelm, M. Antonietti, B. Smarsly, R. Noeske, P. Strauch, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3561.]

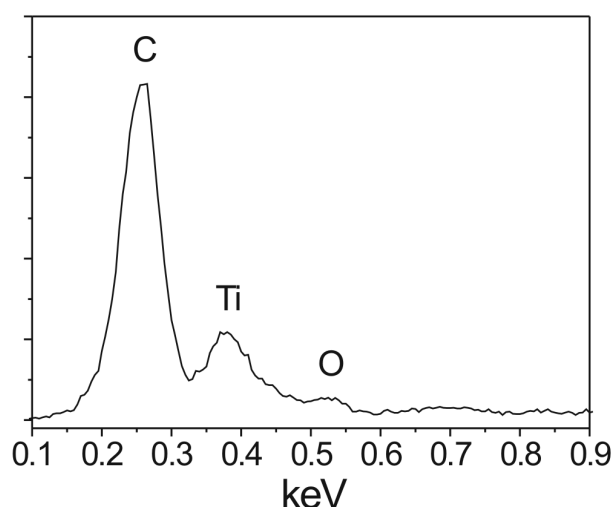


Figure S3. Energy dispersive X-ray (EDX) spectrum of TiC/C with carbide content of about 75 weight percent. After carbothermal reduction of titanium isopropylate infiltrated carbon monoliths at 1400 °C, there is only a miniscule amount of oxygen present in the material; this residual oxygen level is presumably a result of surface oxidation caused by exposure to air (note that the monolithic samples have been stored in air). Thus, the presence of TiOC can be excluded. Moreover, EDX confirms the elemental makeup described in the manuscript and the results obtained by TGA (in particular the carbide content).

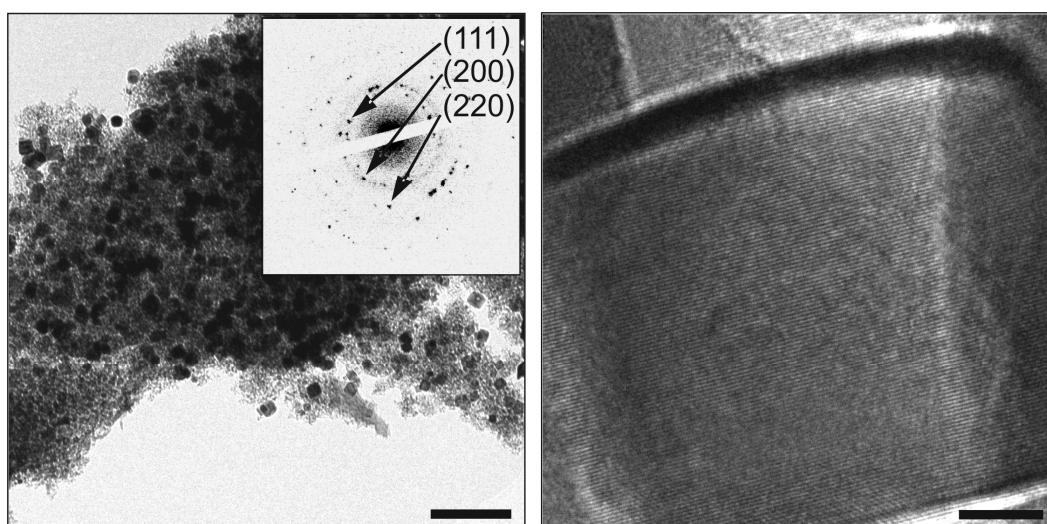


Figure S4. Electron microscope images of TiC/C with carbide content of about 75 weight percent. Left: low-magnification bright-field TEM image showing a

homogeneous distribution of TiC nanocubes in porous carbon. Inset: SAED pattern taken from a region of about 300 nm by 300 nm in size. Lattice spacings calculated from the diffraction spots correspond well with cubic TiC (NaCl structure type). Right: HRTEM image of a single TiC nanocrystal. Scale bars: left - 200 nm, right - 5 nm.