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Low-Temperature Pseudomorphic Transformation of Ordered Hierarchical Macro-mesoporous SiO_2/C Nanocomposite to SiC via Magnesiothermic Reduction

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Three-dimensional SiC nano/microstructures have numerous potential applications in catalyses, high temperature electronic and photonic devices, and the fabrication of micro-electromechanical systems (MEMS), due to their high thermal and chemical stabilities, good thermal conductivity, excellent mechanical properties, and wide-band-gap semiconductor nature.[1] Most of these complex SiC nanostructures are fabricated by two-step templating synthesis methods using preceramic polymers, such as polycarbosilanes, as precursors.[1,2] These syntheses are cost-intensive and time-consuming processes due to the use of special polymers and the high temperature (~1200 °C) pyrolysis process. A better alternative is to first fabricate well-defined silica-based nanostructures at a low cost and then convert them to the corresponding SiC nanostructures without losing structure regularity. It is well-known that SiO_2 can be converted to SiC via the carbothermal reduction process, which uses carbon as a reductant at high temperature (~1400 °C).[3] However, this is not a pseudomorphic transformation process due to the intermediate formation of gas phase SiO, so that the obtained SiC products possess different structures than their SiO_2 precursors. The SiC products are mostly in the form of nanoparticles, nanorods, and nanotubes because of the crystal growth tendencies of SiC.[4]

Herein, we report a low temperature synthesis approach for directly converting SiO_2/C composite nanostructures to the corresponding SiC materials without losing their nanostructure morphologies via a so-called magnesiothermic reduction,[5] which has been utilized for the syntheses of silicon nanostructures from SiO_2 precursors.[6] The overall reaction can be described as $SiO_2 + C + 2Mg \rightarrow SiC + 2MgO$.[5] Crystalline SiC can be obtained by this approach at a temperature as low as 600 °C, only approximately half of that applied in the earlier carbothermal reduction and preceramic polymer pyrolysis methods.[2,3] Neither a high temperature special furnace nor a high purity protection inert gas is required, which greatly reduces the fabrication costs and saves energy. More importantly, this pseudomorphic transformation can be regarded as a general synthesis method for different kinds of SiC nanostructures, and it can also be extended to other metal carbide materials such as TiC. In this research, an ordered hierarchical macro-mesoporous (OHM) SiC material (designed as OHM-SiC) was synthesized for the first time to the best of our knowledge. This morphology is expected to have promise in catalytic applications that require high space-flow velocities, high surface areas, and high thermal as well as chemical stabilities.[7]

The OHM-SiO_2/C precursor was synthesized by using Pluronic F127 block copolymer and polystyrene spheres as dual templates.[8] An SEM image (Figure 1a) shows that the ordered macroporous structure of the prepared OHM-SiO_2/C has pore diameters of ~230 nm. High-resolution SEM (Figure 1a inset) and TEM (Figure S3) images clearly reveal the presence of mesopores in the OHM-SiO_2/C framework. The diameter of these mesopores is ~4.7 nm, as determined by nitrogen sorption analysis. XRD patterns of the OHM-SiO_2/C show one diffraction peak in the low angle range (Figure S4) and one broad peak in the high angle range (Figure 1e), indicating that it has an ordered mesostructure with an amorphous framework. TGA analysis (Figure S6) gives the weight percentages of silica and carbon in OHM-SiO_2/C as 71 and 29 wt %, respectively.

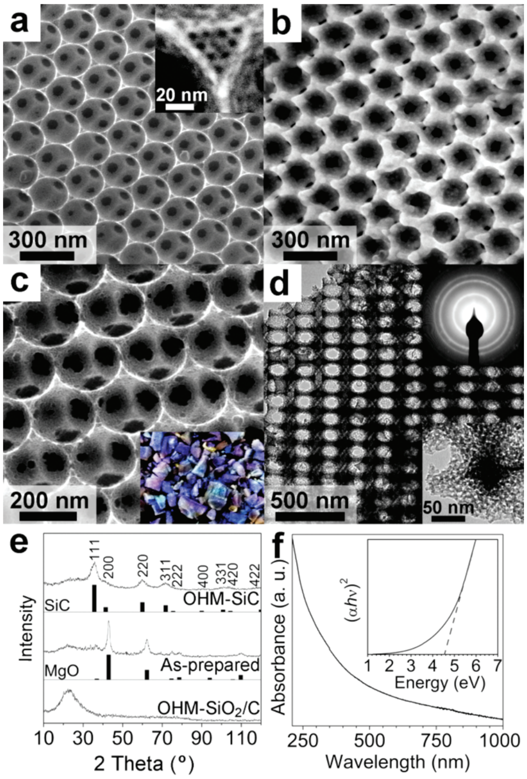

Figure 1. SEM images of (a) OHM-SiO_2/C precursor, (b) as-prepared sample with MgO byproduct, and (c) OHM-SiC product; inset is an optical image that shows its structural color. (d) TEM images and SAED pattern of OHM-SiC. (e) XRD patterns of OHM-SiO_2/C, as-prepared sample, and OHM-SiC. (f) UV−vis spectrum of OHM-SiC.

OHM-SiO_2/C was mixed with magnesium turnings, sealed in an iron tube, and heated to 700 °C for 12 h in a tube furnace for the magnesiothermic reduction. The XRD pattern of the as-prepared product

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(Figure 1e) shows several intense diffraction peaks. Most of these can be indexed to magnesia, which is the main component of the as-prepared sample (>50 wt %, estimated from the reaction equation). A trace amount of Mg_2Si was also detected from the XRD pattern, consistent with what has been observed in the magnesiothermic synthesis of Si.[6] MgO and Mg_2Si were both removed by a 2 M HCl washing. The XRD pattern of this OHM-SiC final product shows several broad but clear diffraction peaks (Figure 1e), which can be indexed as the cubic 3C-SiC phase (JCPDS: 65-0360), namely β-SiC, indicating that the amorphous silica precursor was successfully transformed to crystalline SiC. XRD patterns of the products synthesized at different reaction temperatures (Figure S7) clearly show that SiC can be synthesized from a minimum of 600 to 800 °C.

The ordered macroscale structure is fairly well retained after the reaction as shown by its SEM and TEM images (Figure 1c, 1d). The diameter of the macropore is still ~230 nm, indicating that no detectable structural shrinkage occurred. This can be attributed to the rigid framework of carbon acting as a stable support. An optical image of OHM-SiC dispersed in ethanol (Figure 1c inset) clearly shows the photonic structural color due to its macrostructure ordering.

A selected area electron diffraction (SAED) pattern (Figure 1d inset) shows three clear concentric rings that can be indexed to the (111), (220), and (311) diffraction peaks of β-SiC, confirming the crystalline nature of OHM-SiC. TEM observation (Figure 1d) and nitrogen sorption analyses (Figure S8) confirmed the mesoporosity of our prepared OHM-SiC. Calculations based on the nitrogen sorption isothermals give a BET surface area of ~410 m^2/g and a pore size distribution of 2.0 to 7.0 nm. Small-angle XRD analysis and TEM observations both showed that the mesostructure, while still present, was partially collapsed and its long-range ordering was greatly diminished.

The final product is primarily composed of silicon and carbon, without magnesium, as revealed by energy-dispersive X-ray spectroscopy (EDX) analysis (Figure S9). A trace amount of oxygen (<5 wt %) was also detected, which may partly come from surface water and oxygen adsorption. TGA analysis (Figure S6) shows that there is ~8 wt % free carbon present in the final product, which can be further removed by burning in air at 500 °C for 5 h (Figure S10). UV−vis absorbance spectroscopy was used to evaluate the optical properties of the prepared OHM-SiC material (Figure 1f inset). The direct band gap is estimated to be 4.6 eV, which is less than the literature values for bulk 3C-SiC (5.3 eV), by extrapolating the linear region of a plot of $(\alpha h\nu)^2$ vs ($h\nu$). The narrowing of the band gap may be because the obtained product is not precisely stoichiometric SiC.[9]

It is significant that crystalline SiC can be directly fabricated at such a low temperature (600 °C) via solid reaction from a silica precursor at normal pressure. Yamane et al. have reported the sodium catalyzed synthesis of β-SiC at 700 °C, in which silicon was used as a precursor.[10] Sandhage et al. also have recently reported that the silica nanostructure can be reduced to the corresponding nanostructured silicon by magnesium at ~650 °C.[6] Based on these literature reports and our results, we presume a two-step reaction mechanism for our synthesis: In the first step, silica is reduced to silicon *via* the magnesiothermic reduction ($SiO_2 + 2Mg \rightarrow Si + 2MgO$), in which Mg acts as a reductant.[6] Our results clearly show that silica is not reduced by carbon *via* the carbothermal reduction ($SiO_2 + 3C \rightarrow SiC + 2CO$). Otherwise at least 36 wt % carbon is required due to the release of CO, which is significantly higher than the carbon content in our OHM-SiO_2/C precursor (29 wt %). In addition, there was no evidence of CO being produced during the reaction. In the second step, the obtained silicon reacts with carbon to form crystalline SiC ($Si + C \rightarrow SiC$).[10] Although Mg is not a reagent in the second step, it is still indispensable because SiC can only be formed above 1200 °C from carbon and silicon if no metal catalyst is present.[11] Therefore, we believe Mg plays a catalytic role in the second step. The uniform distribution of silica and carbon in our composite precursor[8] makes it possible for the silicon intermediate to directly react with nearby carbon species in the second step, making the SiO_2/C to SiC conversion a feasible macroscale pseudomorphic transformation. The magnesium has some mobility during the reaction (the melting point of bulk magnesium is 650 °C), which may explain the reason for the decrease of long-range mesostructure regularity after the reaction.

Besides SiC, there are numerous other carbides that possess unusual properties and have attracted considerable interest as nanostructures.[12] With this in mind we also tested the magnesiothermic synthesis of an OHM-TiC material following a synthetic procedure similar to that for SiC. XRD analysis as well as SEM and TEM investigations (Figures S11−14) clearly reveal that an ordered hierarchical macro-mesoporous crystalline cubic phase TiC can be analogously synthesized by using the corresponding OHM-TiO_2/C composite as a precursor.

In conclusion, we present here a low temperature process for pseudomorphic transformation of silica-based nanostructures to the corresponding SiC nanostructures via magnesiothermic reduction. The approach is expected to be a general method for various nanostructured metal carbide materials.

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Supporting Information Available: Experimental details and sample characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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