Supplemental Information for:

Gentle Reduction of SBA-15 Silica to its Silicon Replica with Retention of Morphology

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Experimental Details

To prepare the SBA-15, 2 g of Pluronic P123 was dissolved in 60 ml (or 360 ml, for SBA-15 nanorods) of 2 M HCl at 38 ºC. Tetraethylorthosilicate (TEOS, 4.2 g) was added into the above solution and vigorously stirred for 6 min. The solution was allowed to stand (quiescent) for 24 hrs at 38 ºC, and then it was subsequently heated at 100 ºC for another 24 hrs in an autoclave. The SBA-15 was collected by centrifugation, dried, and calcined at 550 ºC in air. Nanosized SBA-15 was prepared similarly, but employing a dilute solution of P123 and TEOS in an acidic aqueous medium under static conditions, as reported in reference 20.

Syntheses of Mg_3Sb_2 and Mg_2Si intermetallic crystals were carried out by solid state reactions, using a mixture of the elements that were heated as pelletized mixtures under Ar at 610 °C for 5 hrs to form the target compositions. Mg and Sb powder were obtained from VWR, and bulk Si (325 mesh) was obtained from Sigma Aldrich. Stoichiometric Mg with Sb (3:2) or Mg with Si (2:1) were mixed and ground in the glovebox before the power was pressed into a pellet. Residual oxygen in the Ar flow was gettered upstream of the gas flow.

The obtained intermetallics were ground into a fine powder before they were mixed with the SBA-15 samples for the reduction. Typically, a two-fold stoichiometric excess of the intermetallic was mixed with SBA-15 in order to achieve full conversion, and the mixture was

well ground and pressed into a pellet. The reaction mixture pellet was then heated at 800 °C for 5 hrs under an Ar flow. After heating, the product mixture for the reaction between Mg_3Sb_2 and SiO_2 was rinsed in *aqua regia* in order to remove the resulted Sb metal and MgO. The obtained Si replica was filtered and rinsed with water before drying for analysis. The product mixture for the reaction between Mg_2Si and SiO_2 was soaked and stirred in 1.0 M HCl for 12 hours. In order to separate the bulk silicon from the decomposition of Mg_2Si from the nanosized silicon replica from SBA-15 nanorods, the HCl/Si suspension was sonicated for 6 hrs before the suspension was settled without disturbance for 1 hr. The upper light suspension that contained the nanorod silicon replica was pipetted and collected by centrifuging.

All materials were characterized using XRD, electron microscopy and BET. X-ray diffraction patterns at low (0.75 to 4º in 2θ) and wide angle (from 20 to 80º in 2θ) were collected on a D8-ADVANCE powder X-ray diffractometer operating at 40 kV and 30 mA and employing Cu-Kα radiation (λ = 0.15406 nm). SEM images were obtained using a LEO 1530 field emission scanning electron microscope. TEM images were collected on a FEI Titan™ 80-300 equipped with an aberration corrector of the imaging lens. The N_2 sorption-desorption isotherms were measured at -196 °C by using a Quantachrome Autosorb Surface Area Analyzer.

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List of Figures:

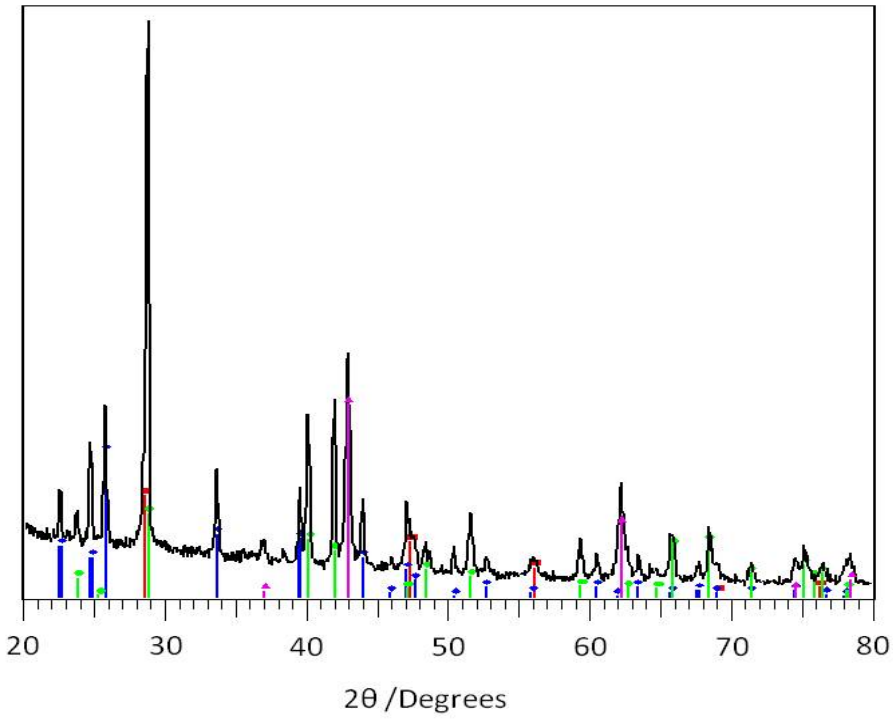


Figure S1. XRD pattern of the unwashed reaction product of Mg_3Sb_2 and SBA-15. Red marks: Si, blue markers: Mg_3Sb_2, green markers: Sb, purple markers: MgO.

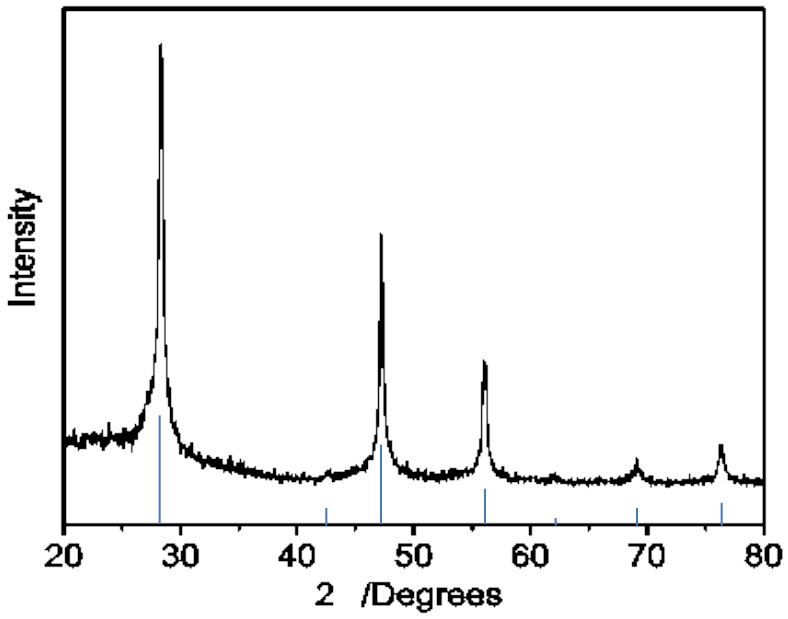


Figure S2. Wide angle XRD pattern of Si derived from reaction with Mg_3Sb_2 (washed product), showing the characteristic reflections of cubic Si; two contributions are evident in the non-Gaussian lineshapes that arise from nanocrystallites with different coherence lengths.

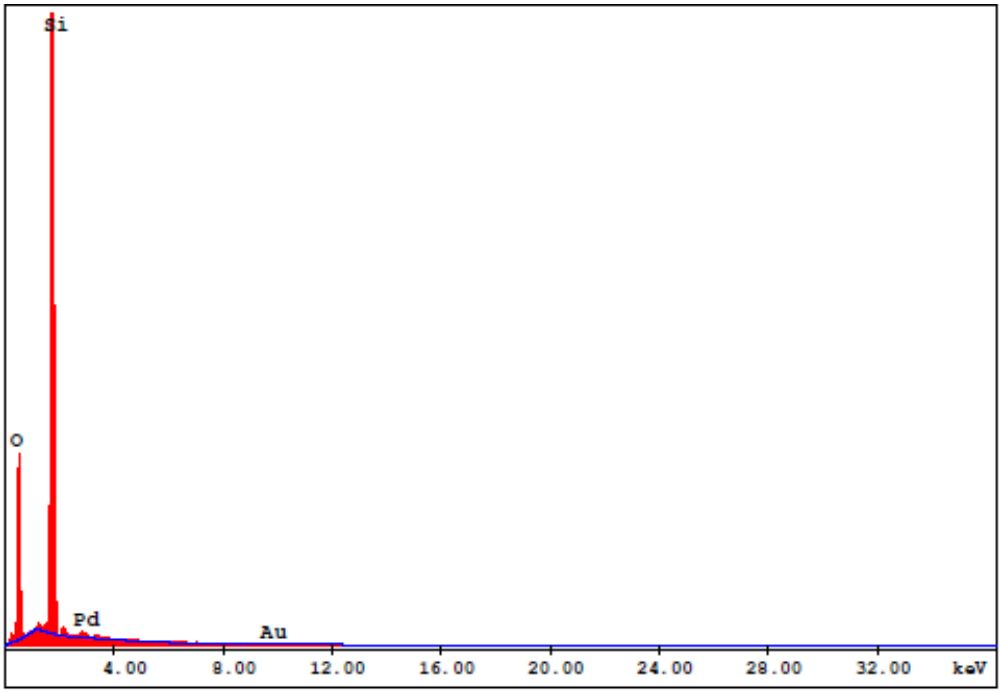
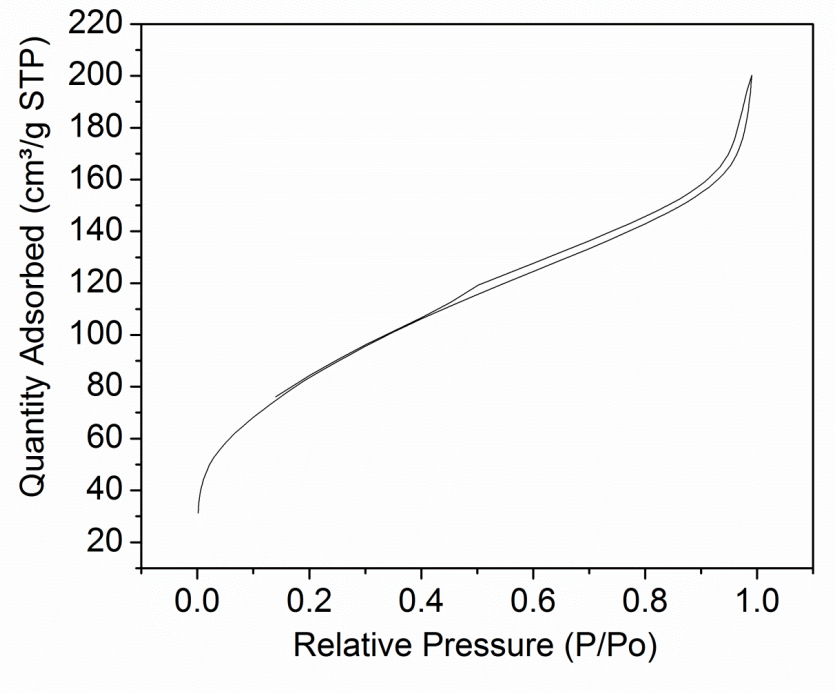


Figure S3. EDAX analysis of the nanorod silicon replica shown in Figure 4b (see text), showing a Si: O ratio of 75: 25. The oxide contribution is presumed to arise mostly from surface passivation of the high surface area nano-silicon.



BET Surface Area Report
BET Surface Area:308.5981 ± 1.4882 m²/g
Slope:0.013873 ± 0.000067 g/cm³ STP
Y-Intercept:0.000233 ± 0.000010 g/cm³
STP C:60.499813 Qm:70.8900 cm³/g
STP Correlation Coefficient:0.9999178
Molecular Cross-Sectional Area:0.1620 nm²

Figure S4. BET isotherm data of Si-MgSi, and BET surface area data.