Innovative nano-applications require the controlled synthesis of one-dimensional (1D) nanostructure topologies and selected polymorphs. Strategies have been developed to rationally synthesize a variety of 1D nanostructures for a broad range of applications utilizing their unique chemical and physical properties. One general strategy uses a metal catalyst seed to confine growth to one dimension via catalyst-assisted chemical vapor deposition processes. Recent studies revealed that the size of the catalyst droplet can change due to the migration of catalyst atoms. This atomic migration during the nanowire growth affects the length, shape, and even the sidewall composition of the nanowires. If the size of a catalyst droplet can be controllably changed during nanowire growth, then modulation of the nanowire’s cross-sectional diameter can be accomplished and thereby create a rich variety of 1D nanostructures. As a practical example, the shrinkage of the metal catalyst during the Si nanowire evolution under high vacuum conditions results in Si nanocone formation. Conical nanostructures are expected to have higher bending stiffness than nanotubes and nanowires and better resistance to thermal-induced drift than nanowires. Hence, they may be superior to nanotube, nanowire, and nanobelt structures for certain applications such as field emission tips, mechanical manipulation at the nanoscale, and scanning probes in surface microscopy and near-field scanning optical microscopy.

Instead of shrinking the metal catalysts, we propose that the enlargement of the catalyst nanoparticle will also create conical structures. Core-shell architectures have been developed for general use as drug carriers for prolonged drug administration as well as multifunctional catalysis. Banhart and co-workers demonstrated that metallic nanocrystals can be expelled from graphite-like carbon shells by electron irradiation and/or in situ heating. Furthermore, the carbon shell protects the encapsulated species from its environment and thereby retaining its intrinsic catalytic properties. Inspired by these previous investigations, we expect that the controlled release of a metal nanoparticle from a graphite-like carbon shell is feasible, where the increasing surface area of the exposed metal nanocrystal can catalyze unusual nanocone and heterostructure formations.

Silicon carbide (SiC) is an important group IV-IV semiconductor for high temperature, high voltage, high frequency, and high power device applications due to its high thermal conductivity, high-saturated electron drift velocity, and high breakdown electric field strength. The strong Si–C bond makes SiC resistant to chemical attack and radiation damage. Nanoelectronic devices based on SiC technology will be more effective and cheaper since no cooling and transformers are needed. However, severe challenges in crystal growth and materials processing limited the development of SiC-based devices. We present herein a “release catalysis” procedure to produce unusual SiC 1D nanostructures and heterostructures by the catalyst-assisted vapor-solid reaction between carbon and silicon monoxide vapor, where the catalysts are iron nanoparticles originally encapsulated in graphite-like carbon shells.

The released iron nanoparticle catalysts were prepared by the catalytic pyrolysis of toluene by ferrocene. Figures 1(a) and 1(b) are scanning electron microscope (SEM) and transmission electron microscope (TEM) images, respectively, of the iron nanoparticles encapsulated within graphite-like carbon shells. Crystalline SiC nanocones and heterostructures were created by the reaction between the graphite-like carbon-encapsulated iron nanoparticles and silicon monoxide vapor generated from a mixture of Si and silica at 1300 °C in an argon atmosphere. The resultant crystalline SiC nanocones and heterostructures are shown in Fig. 1(c). Figure 1(d) is a high resolution TEM (HRTEM) image of the tip of a SiC nanocone. The SiC is face-centered cubic with (111) lattice spacing of 0.25 nm surrounded by a <1 nm thin amorphous SiO2 layer. The HRTEM images of the SiC nanocones also reveal a high density of striations perpendicular to the nanocone axis, corresponding to nanoscale twins and/or stacking faults consisting of several atomic lay-
The presence of nanoscale twins should lead to a dramatic increase in the SiC strength, ductility, and hardness due to the decrease in the average distance that a dislocation needs to travel from one twin boundary to another during plastic deformation. The existence of a catalyst droplet at the thicker end of the SiC nanocone suggests that the growth may follow the vapor-liquid-solid growth process. Furthermore, the diameter of a nanowire is determined by the size of the catalyst droplet which one would expect to be similar in size to the original catalyst seed. Intriguingly, the catalyst droplet at the thicker end of a SiC nanocone with an average size of 12 ± 6 nm is over an order of magnitude larger than the original nanocatalyst seed with an average size of 1.2 ± 0.25 nm. Also, the average tip size of the SiC nanocones is approximately twice that of the initial iron nanocatalyst seed. These observations imply that the graphite-like carbon shell does confine the metallic nanocrystal, where the tip size of the nanocones can be controlled by the size of the originally encapsulated metal nanoparticles. However, the size of the catalyst droplets, which increases by over a factor of 30, demonstrates that the catalyst droplets must agglomerate during the evolution of the SiC nanocones. The released iron nanocrystal from graphite-like carbon shells has a larger surface area to volume ratio than the larger clusters. Thus, the nanocrystal can form larger nanoclusters by the capture of other released iron nanocrystals as driven by the lowering of the total surface free energy, such as by the Ostwald ripening effect. Since the size of a nucleated iron droplet gradually increases, the diameter of the growing nanowire that is being catalyzed by the iron droplet will increase as well and ultimately form a nanocone, as illustrated in Fig. 2(c). The release and agglomeration behaviors of iron nanoparticles were supported by in situ TEM annealing experiments, where TEM images of the carbon-encapsulated iron nanoparticles were taken before and after annealing at ~600 °C inside the TEM column. After annealing, bare iron nanoparticles with similar sizes as the originally encapsulated iron nanoparticle (~12 nm) corresponding to empty graphite-like carbon shells and very large iron clusters with sizes of several hundreds of nanometers were observed, indicating that iron nanocrystals escaped from the graphite-like carbon shell and combined to form large iron nanoparticles. In contrast, Hannon et al. reported Si nanocone formations due to the gradual shrinkage of the gold catalyst via surface diffusion under high vacuum condition. However, Cao et al. suggested that catalyst adatoms may migrate through vapor phase dissociation as well. Our result provides another scenario for catalyst migration, where the catalyst droplet enlarges due to agglomeration as energetically driven by the reduction in the total surface area.

The enlargement rate of the iron nanoparticles is not uniform, as can be deduced from the presence of multisegmented SiC heterostructures. Figures 3(a)–3(c) are TEM images of modulated nanocone structures where segments of SiC with uniform or slowly increasing diameters are separated by an abrupt change in diameter. One such SiC nanocone, consisting of a nanocone segment with a length of 520 nm and an apex angle of 3° ~5°, as well as a second cylindrical segment with a uniform diameter of 60 nm and a length exceeding 2.5 μm, is displayed in Fig. 3(a). Figure 3(b) reveals a 1D SiC nanostucture consisting of two cylindrical segments with diameters of 90 and 240 nm joined by a 250 nm nanocone section with a slope of 20°. Figure 3(c) shows a nanocone consisting of three segments, where the initial segment is cylindrical with a uniform diameter of 40 nm. The second and third segments are conical with slopes of 2° and 5°, respectively. The evolution of the length of the nanocone as a function of the calculated catalyst size is shown in Figs. 3(e)–3(g). These profiles provide critical insights on the evolution of the individual iron nanoparticles since the changing diameter of the SiC nanocone reflects the
size changes in the iron catalyst. The iron droplets may enlarge gradually due to the continuous supply of iron atoms to form ideal nanocone shapes, coalesce with neighboring droplets leading to an abrupt change in the SiC diameter, or stop growing to form a uniform cylindrical SiC section. These profiles depict the rich variety of 1D nanostructures produced by the released catalysis route. More generally, this released catalysis approach should be readily applicable to other metal-catalyzed vapor-solid reactions to create unusual conical shapes and heterostructures of different materials.

Discovery of innovative pathways for nanomaterial synthesis is essential to the development of nanocrystal topologies and polymorphs with unique properties and applications. By means of the reaction between core-shell structured carbon-encapsulated iron nanoparticles and silicon monoxide vapor generated from the mixture of silicon and silica at 1300 °C, SiC nanocones and heterostructures have been synthesized. The most important feature of our observations is the continuously changing cross-sectional diameters of the SiC nanocones. This is related to the enlargement of the metal catalyst due to the thermally induced release of iron nanoparticles from the graphite-like carbon shell and the agglomeration of the released Fe nanoclusters. The SiC nanocones may find important applications in nanotechnology, such as nanoscale cantilevers, probes, and light-emitting diodes. Various SiC heterostructures may be integrated into logic nanodevices for reliable gas sensors and nanoelectronics. We hope that this work will generate further interest in the released catalysis method and enable further developments in the shape and structural dependent properties of semiconductor nanocones and their heterostructure.

This research was supported in part by grants from the NSF (Grants No. NER-0508238 and DMR-0804892). L.C. and Z.L. thank the Alexander von Humboldt foundation for the fellowships.

15 D. L. Huber, Small 1, 482 (2005).
26 W. Z. Ostwald, Phys. Chem. 34, 495 (1900).