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Electronic supplementary information

Amorphous Carbon Coating for Improving Field Emission Performances of SiC Nanowire Core

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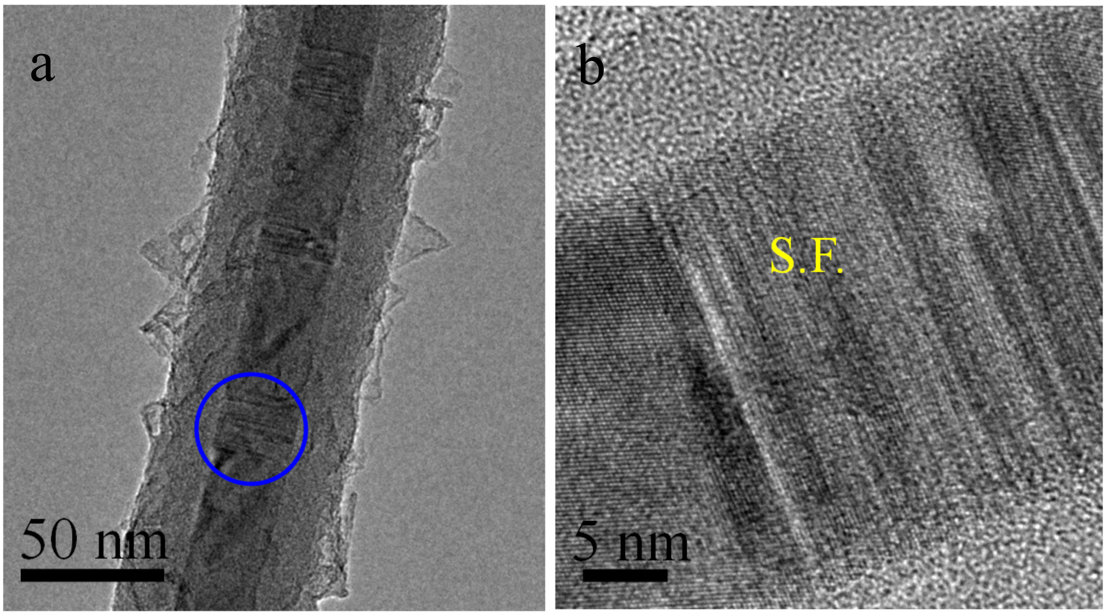

Fig. S1 Traditional TEM images of a) SiC@a-C coaxial nanocables, respectively. The SAED and EDS patterns taken from the corresponding areas have been inserted. b) The HRTEM image of SiC@a-C coaxial nanocables taken from the corresponding area.

Fig. S1a is a typical TEM image of a single SiC@a-C coaxial nanocable with different phase contrast. The coating layer is a-C (the outer light area) with the thickness of 20~30 nm and the core is SiC nanowire (the inner dark area) with the diameter of approximately 25 nm respectively, which presents that the as-synthesized product has numerous randomly distributed sharp bumps along the axial direction throughout the nanocable. Fig. S1b presents a representative high-resolution transmission electron microscopy (HRTEM) image of the SiC nanowire core, recording from the marked area of Fig. S1a. Being absolutely consistent with XRD pattern, some stacking faults (S.F.) can also be obviously observed in HRTEM image recorded from the marked area of a single SiC@a-C coaxial nanocable.

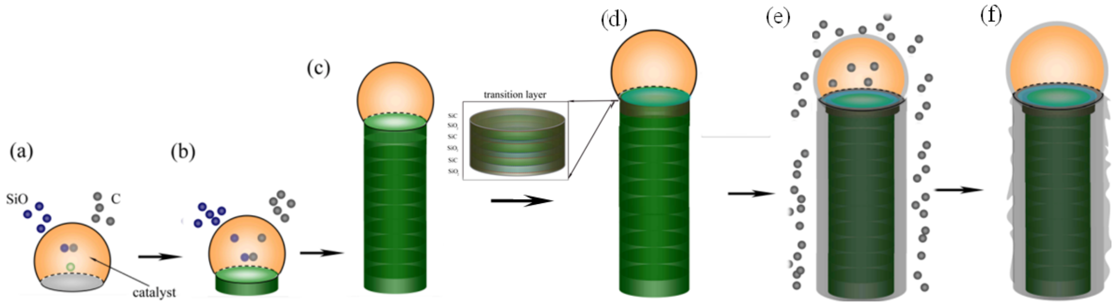

Fig. S2. Schematic of growth process of the SiC@a-C coaxial nanostructures

During the synthesis of SiC@a-C coaxial nanocables under excess C atmosphere, the growth mechanism could be described as follows:

The SiO (V) was firstly generated by a solid-solid reaction between milled Si and SiO_2 powders:

$$\mathrm{Si\ (V) + SiO_2 = 2SiO\ (V)} \tag{1}$$

Secondly, abundant C (V) was generated by the pyrolysis reaction 2 when continuous and steady CH_4 gas was injected into the furnace during insulation stage:

$$\mathrm{CH_4 = C\ (V) + 2H_2} \tag{2}$$

Subsequently, small amount of CO gas was generated via an incomplete reaction between generated C (V) and residual O_2:

$$\mathrm{2C + O_2 = 2CO} \tag{3}$$

Meanwhile, the catalyst droplets (marked as M, the corresponding chemical valence is X^+) in nanoscale were reduced by generated C:

$$4M(NO_3)_x = 2M_2O_x + 4xNO_2 + XO_2 \tag{4}$$

$$2M_2O_x + XC\ (V) = 4M + XCO_2 \tag{5}$$

At the beginning of the aeration stage, the generated SiO (or residual Si) and C (or CO) were dissolved in the nano-catalyst droplets to form alloy system (Fig. S2a). To the best of our knowledge, more C atoms were absorbed and dissolved in the liquid Fe-Ni catalyst droplet than using Ni catalyst, because the Fe had higher absorbent ability for C. With the increase of the concentrations of SiO (or residual Si) and C (or CO) in the system, they would become super-saturation, and the following reactions (6~10) should be considered between silicon (SiO or Si) and carbon atmospheres (C or CO) in the catalyst system at 1250 °C:

Table 1 Calculated values of ΔH, $T\Delta S$ for ΔG for SiO_2 and SiC synthesis at 1250 °C

Reaction no.	Reaction	ΔH/kcal	$T\Delta S$/kcal	ΔG/kcal
(6)	$2SiO\ (V) + 3C = 2\ SiC + CO_2$	-2478.344	-985.337	-1492.910
(7)	$Si\ (V) + C\ (V) = SiC$	-1235.142	-472.224	-762.871
(8)	$CO_2 + C\ (V) = 2CO$	-553.493	19.494	-572.990
(9)	$2Si\ (V) + CO = SiO\ (V) + SiC$	-954.365	-461.527	-492.792
(10)	$3SiO\ (V) + CO = SiC + 2SiO_2$	-1429.300	-1017.745	-411.454
(11)	$SiO_2 + 3C\ (V) = SiC + 2CO$	-1559.228	-215.509	-1343.698

Considering their ΔG values ($\Delta G_6<\Delta G_7<\Delta G_8<\Delta G_9<\Delta G_{10}$) and relative concentration of the components in the furnace ($C_{SiO}>C_{Si}>C_C>_{CO}$), we thought that the growth of SiC nanowires was predominated by the reaction 6 and 7 (Fig. S2b). Then, the CO_2 generated from the reaction 6 reacted with residual C to form CO gas, as shown in reaction 8. The interactions between SiO (or Si) and CO took place (reactions 9 and 10), and SiO_2 was formed by reaction 10. Being different from the synthesis of SiC@SiO_2 coaxial nanocables, the generated C would further react with the SiO_2 to form SiC and CO according to reaction 11. Therefore, the SiO_2 was consumed in a carbon-rich atmosphere, and only SiC nanowires were precipitated from the catalyst liquid droplet (Fig. S2c and S2d). As reaction time was prolonged, SiO would be exhausted. Subsequently, residual C atoms could randomly adsorb on the surface of the obtained SiC nanowires (Fig. S2e). With the rapid decrease of the temperature, the adsorbed C atoms would solidify and form amorphous carbon coatings around SiC nanowires. Finally, the SiC@a-C coaxial nanocables could be obtained when the furnace was naturally cooled down to room temperature (Fig. S2f).