SUPPLEMENTARY INFORMATION

A Novel Combined Experimental and Multiscale Theoretical Approach to Unravel the Structure of SiC/SiO_x Core/shell Nanowires For Their Optimal Design

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This supplementary information reports further computational details and experimental data on the topics developed in the main text of this work, including: modeling of realistic SiC/SiO_x core/shell nanowires (NWs), simulation of XANES spectra based on these topologies, and additional XANES experimental spectra.

1. Computational details on nanowire structural modeling

1.1. Influence of the radius size and of the surface termination on 3C-SiC nanowires

The SiC nanowires (NWs) were obtained by cleaving a cilinder out of a 3C-SiC supercell along the [111] direction, which represents the growth axis in our synthesis process. The first observable that we assess is the band gap of the SiC NW versus the diameter of the wire. In particular, three NWs with diameters of 1.2, 1.8 and 2.6 nm were modeled.



Figure S1: Transverse view of the three SiC core NWs investigated in this work. The NWs diameters are 1.2, 1.8, and 2.6 nm respectively.

To study the electronic properties, we saturated the surface bonds with -H atoms or with -OH (hydroxyl) groups. Structural optimization and electronic band structure simulations were carried out by using the SCC-DFTB method [1]. The total Density of States (DOS) of SiC NWs was computed and compared to 3C-SiC bulk in Fig. S2, to assess the influence of quantum confinement on the electronic properties. We notice that for hydrogenated SiC NWs, the band gap tends to the bulk value, which is 2.3 eV from DFTB simulations (experimentally is reported to be 2.36 eV).

Of course, the DOS of these nanoscale systems dramatically depends on surface termination. Notably we obtain, as reported in Fig. S3, a smaller band gap using -OH instead of -H to passivate the NW surface.



Figure S2: Total DOS of the three different diameter (d) NWs saturated by -H atoms: a) d=1.2 nm ; b) d=1.8 nm; c) d=2.6 nm; d) bulk system

These findings are in agreement with what reported in Ref. [2], where the authors observe a decrease of the band-gap of Si/SiO_2 core-shell quantum dots moving from -H to -OH saturation. To explain this different trend with passivating agents we perform a Mulliken charge distribution analysis. Mulliken charges of C and Si atoms are plotted in Fig. S4 and S5, respectively.

We observe that surface atoms, in particular the carbon atoms in Fig. S4, show a different behaviour for different terminations. This effect influences the electronic properties, such as the band gap, and the Projected Density of States (PDOS). The latter are reported in Figs. S6 and S8. We notice that p orbitals of oxygen atoms contribute to the top of the valence band only in the -OH case, while the lower energy conduction states for both -H and -OH terminations are mainly composed by p- and d- hybridized silicon orbitals. This reduces the band gap in -OH terminated NWs.

In order to further investigate the effect on the electronic properties of passivating with -H and -OH the SiC NWs we performed the calculation of the probability densities of the top of the valence band (VBM) and of the minimum of the conduction band (CBM) in the smallest radius -H and -OH terminated NWs. The plots (isovalue 0.0006 a.u.) of these probability densities (square modulus of the wave functions) are reported in Figs. S10 and S11. We notice that both the VBM (left hand side of Fig. S10) and the CBM (right hand side of Fig. S11) is strongly localized on the surface (notably on the oxygen atoms) and the CBM (right hand side of Fig. S11) remains localized in the NW core.

Finally, from our simulations we conclude that two main factors affect the NWs electronic properties: quantum confinement and passivation. These two effects are counteracting: the first broadens the gap, the



Figure S3: Comparison of the total DOS between d=1.2 nm (a,d), d=1.8 nm (b,e), and d=2.6 nm (c,f) NWs, saturated by H atoms (a,b,c) and by -OH groups (d,e,f).



Figure S4: Mulliken charge distribution analysis of carbon atoms (colored atoms) in the SiC NWs with diameters 1.2 (left panel) and 1.8 (right panel) nm. In both figures the nanowire in the left hand side is -H terminated while in the right side is -OH terminated. The charge scale starts from 3.6 (dark) to 4.4 (white).



Figure S5: Mulliken charge distribuition analysis of silicon atoms (colored atoms) in the SiC NWs with diameters 1.2 (left panel) and 1.8 (right panel) nm. In both figures the nanowire in the left hand side is -H terminated while in the right side is -OH terminated. The charge scale starts from 3.6 (dark) to 4.0 (white).

latter makes it smaller when a -OH termination is used instead of hydrogen. In the text of our manuscript we thus carefully discuss these two mechanisms.



Figure S6: Total and Projected DOS of SiC NWs with diameter equal to 1.2 nm for both -H (left) and -OH (right) terminations



Figure S7: Band structure of SiC NWs with diameter equal to 1.2 nm for -H (left) and -OH (right) terminations.



Figure S8: Total and Projected DOS of SiC NWs with diameter equal to 1.8 nm for both -H (left) and -OH (right) terminations.



Figure S9: Band structure of SiC NWs with diameter equal to 1.8 nm for -H (left) and -OH (right) terminations.



Figure S10: Left) Square modulus of the wave function of the VBM. Right) Square modulus of the CBM wave function. The plots are both referred to the 1.2 nm diameter -H-terminated SiC NW.



Figure S11: Left) Square modulus of the wave function of the VBM. Right) Square modulus of the CBM wave function. The plots are both referred to the 1.2 nm diameter -OH-terminated SiC NW.

1.2. Adding the silica shell to 3C-SiC NW core and the strategy for SiC/Silica interface modeling

To model the SiO_x outer shell, we coated the 0.6 nm radius SiC core NW. This choice was basically due to the large computational cost of dealing with wires of larger diameter. The LAMMPS program suite, implementing molecular dynamics with reactive potentials (ReaxFF) tailored to reproduce realistic silica and silicon carbide structures [3], was used to build the SiC/SiO_x NW architecture. Nevertheless, an approach purely based on molecular mechanics is not capable to deliver an accurate representation of the interface between the SiC core and the silica outer shell. In particular, a major problem is related to the description of the decreasing density moving along the radius from the SiC core to the SiO_2 shell. Indeed, the atomic and bond density of the SiC core is much higher than that of silica shell and molecular dynamics cannot be efficiently used to reproduce this effect. To overcome this problem, we decided to use an hybrid approach, in which the bond density is manually decreased by a factor of 2.3 from 42 to 18, using a three-step procedure as exemplified in Fig. S12. This result is reached by saturating the SiC core surface dangling bonds (such as those labeled a, b and c) with oxygen atoms (labeled 1, 2 and 3), by adding a three-coordinated silicon atom (labeled 4) and a further oxygen atom (labeled 5) bound to silicon. This construction was performed saturating 18 free bonds. The others 24 free bonds were saturated two by two, first with oxygen atoms (in a similar way to the previous case), then inserting the Si-O group and finally bridging these three-coordinated silicon atoms two by two with an oxygen atom.



Figure S12: Interfacial bond density reduction procedure. Left panel: our strategy to reduce progressively the number of SiC core surface bonds to that of silica shell can be divided into three steps. First, we saturate all the surface dangling bonds (for example those of atoms indicated by a and c) by oxygen atoms (labeled 1,2,3). Second, a silicon atom (labeled 4) was placed in the proximity of these oxygen atoms in such a way to be three-coordinated. Finally, a further oxygen atom (labeled 5) was bound to silicon. Right panel: a transverse view of the NW core showing the bonds at interface.

As a further step, the silica outer shell was created on the top of the interfacial region by using molecular dynamics. This procedure was accomplished by defining a 3 nm side periodic tetragonal cell surrounding the SiC core and the interface (see Fig. S13). Moreover, silicon and oxygen atoms were added to the simulation cell in 1:2 stoichiometric ratio to reach a density of 2.20 g/cm³. SiC and interfacial atomic regions were clamped down while annealing the outer SiO_x shell at 4000 K for 100 ps. Subsequently the temperature was decreased to 10.0 K in 100 ps (using 1 fs timesteps). In the last step of our procedure both the SiC core and the interfacial regions were released and the NW structure was further optimized by DFTB to reach forces among atoms below 0.05 eV/Å.



Figure S13: Computational cell used to add the silica outer shell on the top of the SiC core. A number of silicon and oxygen atoms were inserted in the 3 nm side periodic tetragonal box to obtain a mass density of ~ 2.20 g/cm³. Finally, the SiC/SiO_x NW has been cut out with a proper choice of shell thickness.

Finally, the SiC/SiO_x NW was obtained by deleting all the atoms that are distant from the wire symmetry axis more than the desired radius. Dangling bonds at the shell surface and some other possibly left within the NW, were passivated by hydrogen atoms.

1.3. Characterization of bond lengths and angles of the SiC/SiO_x core/shell NW model



Figure S14: Characterization of SiO_x sample: on the left hand side we plot the distribution of a given radial distance between Si and O atoms; on the right hand side the O-Si-O angles

Geometry characterization of the SiC/SiO_x core/shell NW model was achieved by computing the following quantities:

- 1. the bond length of Si-O bonds (SiC core keeps its crystalline structure)
- 2. the bond angles forming O-Si-O atoms

In the left hand side of Fig. S14 we plot the distribution of a given radial distance between Si and O atoms; on the right hand side the O-Si-O angles in the same sample. The peaks compare well with those of silica [4, 5, 6].

1.4. Density of States of SiC/SiO_x core/shell NW

While our SiC/SiO_x NW computational model cannot be realistic due to the large dimensions of a real NW, however provides interesting and reliable information on the electronic band structure of the system, particularly obtained by analyzing the total DOS. Interestingly we notice that the SiC/SiO_x NW show a band gap equal to that of the same dimension SiC core NW saturated by -OH groups. This can be rationalized by noticing that in the SiC/SiO_x NW the very first layer in close contact to the SiC core contains oxygen atoms. In Fig. S15 we report both the total and projected (orbital-resolved) DOS. PDOS will be useful in the interpretation of XANES spectra to identify the transitions.



Figure S15: Total and Projected Density of states of our SiC/SiO_x NW model

2. XANES spectra

2.1. SiC bulk XANES spectra simulations

X-ray absorption spectra of the C, O and Si K-edge of the SiC/SiO_x core/shell NW were investigated. To perform these simulations we used the program XSpectra [7, 8], which is part of the Quantum Espresso suite code [9]. XSpectra is able to simulate X-ray absorption dipolar cross sections from the pre-edge to near-edge regions within the single particle approximation. We started our analysis by testing the C K-edge absorption spectra in crystalline 3C-SiC [10]. The geometric structure of bulk SiC used for these calculations is reported in Fig. S16.



Figure S16: Geometric structure of the 3C-SiC bulk cell, having a cell lattice constant of 8.696 Å and containing 64 atoms

The pseudopotentials (PP) used in these calculations are listed in Tab. S1. The DFT cut-off energy for the wavefunctions was chosen 952.35 eV, while 3809.40 eV for the density.

Atom	PP	1s-PP
С	C.pbe-mt-gipaw. UPF	C.star1s-pbe-mt-gipaw.UPF
Si	Si. pbe-van-gipaw. UPF	Si.star1s-pbe-van-gipaw.UPF
0	O.pbe-van-gipaw.UPF	O.star1s-pbe-van-gipaw.UPF
Η	H.pbe- $rrkjus.UPF$	

Table S1: List of pseudopotentials used for the calculations of the XANES spectra.

In the left hand side of Fig. S17 we report a comparison between our simulations and the experimental data by Liu et al. [10], while in the right we compare our theoretical C K-edge spectrum with that one obtained by Liu [10], finding an overall good agreement. In the right hand side of Fig. S18 we report the XANES spectrum of graphene.



Figure S17: Left: comparison between experimental (from Ref. [10], red curve) and our theoretical C K-edge adsorption spectra of bulk SiC crystal (blue curve). Right: comparison between the theoretical (red curve) C K-edge adsorption spectra of bulk SiC crystal (from Ref. [10]) and our simulations (blue curve).

The good agreement between our simulations and experimental measurements for 3C-SiC makes us confident that the same parameters can be safely used to calculate the C K-edge adsorption spectra of a SiC NWs.



Figure S18: Left: Comparison between calculated C K-edge adsorption spectra of $SiC+SiO_x$ and of SiC+OH nanowires. Right: C K-edge absorption spectra of graphene. Differently colored spectra represent the contribution to the total absorption spectrum of the three polarization directions

2.2. Nanowires XANES spectra calculations

Also in the case of SiC/SiO_x core/shell NWs the presence of the above mentioned peak can be related to sp^2 carbonaceous contaminations present in the SiO_x shell, such as a carboxyl defect within the shell. In Fig. S19 we plot the K edge absorption spectra of our SiC/SiO_x core/shell NW model including this defect.



Figure S19: Experimental C K-edge XANES spectrum of as-grown SiC/SiO_x core/shell NWs (red), in comparison with theoretical XANES spectra from our SiC/SiO_x core/shell NW model including a carboxyl defect within the shell.

We notice that by inserting carbonaceous defects in the shell the absorption spectrum presents a different behaviour due to a changed chemical environment of the carbon atoms present in the structure.

2.3. Supporting experimental XANES spectra

Si K-edge XANES spectra of the HF-etched SiC NWs were recorded 1) immediately after the etching process (see red line in Fig. S20a), and 2) after longer exposure to air (about 60 days, see black line in Fig.

S20a). It can be clearly seen that the feature denoted by B^{*} at 1847 eV can be only detected when the HF-etched NWs were immediately analysed after the etching process. In Fig. S20b, the Si K-edge XANES spectrum of SiO_x NWs (without SiC core) is compared to that of as-grown SiC/SiO_x core/shell NWs. It is obvious that the pre-edge peak labeled as A' at 1842 eV is only present in the SiC/SiO_x core/shell NWs. Therefore, it can be reasonably assumed that it originates from the SiC core. We notice that the total electron yield (TEY) mode used to record the experimental XANES spectra is relatively surface-sensitive (i.e., probing depth of a few nm). However, since the SiO_x shell (average thickness of 20 nm [11]) of our as-grown SiC/SiO_x core/shell NWs can be locally thinner than 20 nm, we are able to detect a small contribution of the internal SiC core.



Figure S20: Experimental Si K-edge XANES spectra: (a) HF-etched SiC NWs, which were analysed immediately after the etching process (red), in comparison with a spectrum recorded after longer exposure to air (black); (b) as-grown SiC/SiO_x core/shell NWs (red), in comparison with bare SiO_x NWs grown without SiC core (black).

Additional O K-edge XANES spectra of SiO_x NWs and of (functionalized) SiC/SiO_x core/shell NWs were recorded (see Fig. S21) to support the results from simulations that the pre-edge peak at 530 eV mainly stems from unsatured oxygen. For instance, we can exclude any effects caused by radiation damage, since the SiC/SiO_x core/shell NWs exhibit the pre-edge peak even at acquisition with very low flux ($< 1 \times 10^9$ photons/s) of the incident X-ray beam (see blue line in Fig. S21). Furthermore, after surface functionalization of the NWs with a porphyrin molecule via carboxylic acid functional groups (see red line in Fig. S21), the pre-edge peak clearly increases. These findings support the idea that the pre-edge peak originates from carbon-containing (functional) groups such as carbonyl and/or carboxyl groups.

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Figure S21: Experimental O K-edge XANES spectra of bare SiO_x NWs grown without SiC core (red) collected with high incident photon flux (i.f.), as-grown SiC/SiO_x core/shell NWs (blue) collected with low i.f., and SiC/SiO_x core/shell NWs functionalized with a porphyrin molecule bearing carboxylic acid functional groups (red) collected with low i.f..

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