Controlled Assembly of Sb$_2$S$_3$ Nanoparticles on Silica/Polymer Nanotubes: Insights into the Nature of Hybrid Interfaces

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Silica nanotubes can serve as high aspect ratio templates for the deposition of inorganic nanoparticles to form novel hybrids. However, the nature of the interfacial binding is still an unresolved challenge when considered at the atomic level. In this work, novel nanocomposites have been successfully fabricated by the controlled nucleation and assembly of Sb$_2$S$_3$ nanoparticles on the surface of mercaptopropyl-functionalized silica/polymer hybrid nanotubes (HNTs). The Sb$_2$S$_3$ nanoparticles were strongly attached to the HNTs surface by interactions between the pendent thiol groups and inorganic sulfur atoms. Detailed analysis of the geometric and electronic structure using first-principle density functional theory demonstrates charge transfer from the nanoparticles to the underlying HNTs at the Sb$_2$S$_3$/HNTs interfaces. Formation of a packed array of Sb$_2$S$_3$ nanoparticles on the HNTs results in mixing of the electronic states of the components, and is mediated by the mercaptopropyl bridges between Sb$_2$S$_3$ and the outer layer of the HNTs.

Semiconductor nanomaterials have recently attracted considerable attention due to their novel properties and potential applications in electronic and optoelectronic devices. Among these nanomaterials, antimony trisulfide (Sb$_2$S$_3$) is recognized as a prospective material suitable for solar energy conversion, thermoelectric technologies and optoelectronic devices in the IR region$^{1-5}$. Single-crystal Sb$_2$S$_3$ nanorods have been prepared by sonochemical methods using ionic fluids$^6$, or by solvothermal/hydrothermal procedures involving a variety of xanthate, dithiocarbamate, dithiophosphate and other types of single-source precursors$^7,8$. However, the formation of Sb$_2$S$_3$ nanoparticles using simple chemical methods has not been extensively studied. Moreover, although changes in the crystal morphology, for example from nanorods to complex flower-like arrangements, can be induced by using surfactant-mediated hydrothermal procedures, or by regulating the type of precursor and reaction time employed in solvothermal methods$^9$, the fabrication of spatially patterned, multicomponent (hybrid) materials comprising Sb$_2$S$_3$ nanoparticles has not explored in detail, even though research on hybrid materials has become a key focus in advanced materials research$^{10-15}$. In particular, as demonstrated in other systems such as the decoration of carbon or silica nanotubes with a wide variety of inorganic nanoparticles$^{16-20}$, the possibility of preparing hybrid functional nanomaterials via selectively assembling Sb$_2$S$_3$ nanoparticles on the surface of preformed nanotubular templates should provide a range of new opportunities.

In this paper, we fabricate hybrid nanostructures comprising uniformly packed arrays of Sb$_2$S$_3$ nanoparticles arranged on the silicified outer surface of highly elongated diblock copolymer nanotubes. The thiol-functionalized silica-coated polymer nanostructures are prepared by a non-equilibrium self-assembly process involving the water-induced transformation of particles of a swollen lamellar gel phase comprising poly (ethylene oxide)-b-poly (1,2-butylene oxide) (E$_{16}$B$_{22}$), tetraethoxysilane, and 3-mercaptopropyl triethoxysilane (HS(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$)$^{21}$. The silicified myelin-like hybrid nanotubules (HNTs) are then incubated at room temperature in a water/ethylene glycol reaction solution containing antimony chloride (SbCl$_3$) and thioacetamide (CH$_3$CSNH$_2$) to generate high aspect ratio silica/polymer nanostructures decorated with closely packed arrangements of discrete Sb$_2$S$_3$ nanoparticles. We use a range of physical methods to investigate the structural and morphological aspects of the as-synthesized and thermally treated nanocomposites, and to elucidate the nature of the mercaptopropyl-functionalized silica surface and its interface with clusters of Sb$_2$S$_3$. Moreover, because the hybrid nanocomposites are integrated structures rather than physical mixtures, the role of the interfacial bonding...
Results

Addition of an ethylene glycol solution of antimony chloride to a suspension of thiol-functionalized silica/polymer (E16B22) myelin-like hybrid nanotubules (HNTs) dispersed in aqueous thioacetamide (TAA) produced a lemon-yellow colored solution of soluble \([\text{Sb(TAA)}_3]^{3+}\) complexes that decomposed through nucleophilic attack of water molecules to release \(\text{S}^2^-\) ions. The corresponding increase in supersaturation with respect to the nucleation of \(\text{Sb}_2\text{S}_3\) was associated with the formation of an orange dispersion after 5 min, which turned brick-red when left unstirred for 24 h at room temperature (Fig. 1a). XRD analysis of the brick-red precipitate indicated that the as-synthesized \(\text{Sb}_2\text{S}_3/\text{HNTs}\) nanocomposites were amorphous, whereas subsequent calcination of the hybrid material at 400 °C under \(\text{N}_2\) resulted in a well-crystallized product exhibiting sharp reflections that were indexed to the orthorhombic \(\text{Sb}_2\text{S}_3\) phase \((a = 11.226 \, \text{Å}, \, b = 11.307 \, \text{Å} \text{ and } c = 3.835 \, \text{Å};\) JCPDS File 06–0474, Fig. 1b). Formation of the orthorhombic phase was consistent with other synthetic routes involving solvothermal, hydrothermal, sonochemical or pulsed growth procedures\(^{20,23}\), and was also replicated in control experiments prepared as above but in the absence of the HNTs (Supplementary Fig. S1 and Table S1), indicating that the silicified polymer nanotubes had no effect on the crystallinity of the \(\text{Sb}_2\text{S}_3\) produced by calcination (all the polymer component was decomposed at 350 °C (TGA and DSC data not shown). The as-synthesized \(\text{Sb}_2\text{S}_3/\text{silica}\) product exhibited a broad peak around 290 cm\(^{-1}\) characteristic of amorphous materials, while the calcined product exhibited six characteristic Raman peaks at 150, 186, 249, 291, 371 and 451 cm\(^{-1}\) (Supplementary Fig. S2), in good agreement with previous Raman spectroscopy studies\(^{23}\). The peak around 290 cm\(^{-1}\) and relatively broad peak at 451 cm\(^{-1}\) were ascribed to the \(\text{Sb}_2\text{S}_3\) pyramidal unit with \(\text{C}_3v\) symmetric modes, and symmetric stretching of the \(\text{Sb}-\text{S}-\text{Sb}\) linkage, respectively.

TEM images of the as-synthesized HNTs prepared at a \(\text{Sb:Si}\) molar ratio of 1:1 showed a network of soft, flexible, highly elongated nanostructures, which were ca. 150 nm in diameter and a few micrometres in length (Fig. 2a). High-magnification TEM images showed the presence of discrete nanoparticles that were uniformly assembled on the external surface of the HNTs (Fig. 2b, c). EDX analysis of the \(\text{Sb}_2\text{S}_3/\text{HNTs}\) showed high intensity peaks for S and Sb, along with a negligible peak for Si (Fig. 2d), suggesting that the surface-embedded nanoparticles consisted of amorphous \(\text{Sb}_2\text{S}_3\). Particle size measurements gave a distribution of nanoparticle dimensions across a range from 4 to 13 nm, with an average size of 7.8 nm (Fig. 2e). Significantly, thermal treatment of the \(\text{Sb}_2\text{S}_3/\text{HNTs}\) at 400 °C under \(\text{N}_2\) gave an inorganic silica/\(\text{Sb}_2\text{S}_3\) product that exhibited partial retention of the filamentous morphology of the nanotubular template (Fig. 2f). SAED patterns displayed reflections consistent with well-crystallized \(\text{Sb}_2\text{S}_3\) (Fig. 2g), in accordance with the XRD results obtained from the bulk sample (Fig. 1b).

We investigated the nature of the interfacial interactions through FTIR spectroscopic and XPS analysis. FTIR spectra of the native HNTs showed a strong characteristic peak at 1105 cm\(^{-1}\), consistent with the superimposition of a C–O stretching vibration in the C–O–C structure of the polymer and Si–O stretching vibration in the silica overlayer of the HNTs (Supplementary Fig. S3). Peaks at 2871–2970 cm\(^{-1}\) and 1460 cm\(^{-1}\), corresponding to the polymer C–H stretching and C–H scissor vibrations, respectively, were also observed\(^{21}\). A broad O–H stretching vibration peak was present at 3437 cm\(^{-1}\) (Supplementary Fig. S3a). Significantly, a 22 cm\(^{-1}\) shift of the Si–O stretching vibration from 1015 to 1038 cm\(^{-1}\) was observed in the presence of surface-attached \(\text{Sb}_2\text{S}_3\) nanoparticles, indicating a change in the vibration environment of the Si–O bonds in the as-synthesized \(\text{Sb}_2\text{S}_3/\text{HNTs}\), possibly due to the formation of covalent S–Sb bonds on the surface of the thiol-functionalized HNTs (Supplementary Fig. S3a). The (The electronegativity difference between S (2.58) and Sb (2.05) is only 0.53, and the S–Sb bond length (2.40 Å) is greater than that of S–H (1.35 Å), implying a decrease in the vibration frequency). FTIR spectra of the calcined product confirmed complete loss of the polymer component, and showed no further change in the Si–O stretching frequency from the shifted value of 1083 cm\(^{-1}\), implying that the S–Sb bonds remained intact after thermal treatment (Supplementary Fig. S3b).

XPS measurements were carried out to identify the surface chemical composition and the oxidation state for the as-synthesized \(\text{Sb}_2\text{S}_3/\text{HNTs}\) (Supplementary Fig. S4). In general, no obvious impurities were detected in the XPS survey spectrum (Supplementary Fig. S4a) of the as-synthesized \(\text{Sb}_2\text{S}_3/\text{HNTs}\), which showed only a weak Si 2p
showed O 1s peaks at 532.09 and 533.44 eV that were ascribed to... the high-resolution XPS profile of the O 1s region at 284.79 and 286.24 eV, which were attributed respectively to the

Figure 2 | Morphologies of as-synthesized and calcined Sb$_2$S$_3$/HNTs. (a) TEM images of as-synthesized Sb$_2$S$_3$/HNTs nanocomposites at low magnification. (b) Single HNT coated with uniform Sb$_2$S$_3$ nanoparticles embedded in the surface silica coating. (c) Open end of a single HNT with associated silica matrix and Sb$_2$S$_3$ nanoparticles viewed at high magnification. (d) Representative EDX spectrum. (e) Size distribution diagram of Sb$_2$S$_3$ nanoparticles shown in (b). (f) TEM image of calcined Sb$_2$S$_3$/HNTs at 400 °C under N$_2$. (g) Corresponding SAED pattern.

peak due to the uniform coverage of Sb$_2$S$_3$ nanoparticles on the surface of the HNTs as observed by TEM (Fig. 2). Values for the Sb:S molar ratio of 1:1.51 and 1:1.70 were determined for a control sample of as-synthesized Sb$_2$S$_3$ and Sb$_2$S$_3$/HNTs, respectively, consistent with a stoichiometry of Sb$_2$S$_3$, with surplus sulfur in the latter arising from the HNTs template. The high-resolution XPS profiles of the main constituents (Sb 3d, S 2p, O 1s and C 1s) of the as-synthesized Sb$_2$S$_3$/HNTs nanocomposite surface showed peak positions for both Sb 4d and S 2p at around 33.65 and 162.10 eV, respectively, and the two observed orbital peaks for Sb 3d$_{3/2}$ (529.42 eV) and Sb 3d$_{5/2}$ (538.83 eV) (Supplementary Fig. S4b), confirmed the presence of Sb(III). These values were very similar to those determined in the control sample of amorphous Sb$_2$S$_3$ (Sb 3d, 529.60 and 538.97 eV), implying that the binding energy of Sb 3d remained unchanged before and after assembly on the surface of the HNTs. The S 2p region of the XPS profile for the as-synthesized Sb$_2$S$_3$/HNTs was composed of three contributions (Supplementary Fig. S4c); two main peaks at binding energies of 162.16 and 161.10 eV that were attributed to a single doublet from S–Sb bonds, and a relatively low intensity peak at 163.2 eV from C–SH bonds of the HNTs.

C–C and C–O (or C–SH) contributions of the as-synthesized Sb$_2$S$_3$/HNTs nanocomposite surface showed peak positions for both Sb 4d and S 2p at around 33.65 and 162.10 eV, respectively, and the two observed orbital peaks for Sb 3d$_{3/2}$ (529.42 eV) and Sb 3d$_{5/2}$ (538.83 eV) (Supplementary Fig. S4b), confirmed the presence of Sb(III). These values were very similar to those determined in the control sample of amorphous Sb$_2$S$_3$ (Sb 3d, 529.60 and 538.97 eV), implying that the binding energy of Sb 3d remained unchanged before and after assembly on the surface of the HNTs. The S 2p region of the XPS profile for the as-synthesized Sb$_2$S$_3$/HNTs was composed of three contributions (Supplementary Fig. S4c); two main peaks at binding energies of 162.16 and 161.10 eV that were attributed to a single doublet from S–Sb bonds, and a relatively low intensity peak at 163.2 eV from C–SH bonds of the HNTs. The peak at 162.10 eV showed a local chemical shift compared with that of the control Sb$_2$S$_3$ sample (161.58 eV), consistent with the formation of S–Sb bonds between the thiolated residues of the HNT template and Sb(III) ions on the surface of the assembled Sb$_2$S$_3$ nanoparticles, as also suggested by FTIR analysis (Supplementary Fig. S3). The position of the O 1s binding energy was superposed with that of the S 3d$_{3/2}$ binding energy (Supplementary Fig. S4b). However, a broader high-resolution XPS profile of the O 1s region showed O 1s peaks at 532.09 and 533.44 eV that were ascribed to contributions from C–O/C=O bonds and Si–O/adsorbed H$_2$O, respectively. Observation of the small Si 2p peak at 103.05 eV (Supplementary Fig. S4a), corresponding to Si–O of SiO$_2$, further confirmed the presence of silica under the packed array of Sb$_2$S$_3$ nanoparticles. Deconvolution of the C 1s region showed two peaks at 284.79 and 286.24 eV, which were attributed respectively to the

The optical properties of the as-synthesized and calcined Sb$_2$S$_3$/HNTs were investigated by solid-state UV-vis absorption spectroscopy, which showed absorbance peaks at around 460 or 670 nm, respectively, with the latter comprising an extended absorption edge of about 750 nm (Supplementary Fig. S5a). Direct band gap energies were determined by fitting the absorption data to the direct transition equation$^{29}$, which gave values of 2.10 and 1.67 eV for the amorphous (as-synthesized) and crystalline forms of Sb$_2$S$_3$ (calcined), respectively. The latter value was lower than that of other reports on crystalline Sb$_2$S$_3$ (1.78–2.50 eV)$^{29}$, suggesting that the Sb$_2$S$_3$/HNTs nanocomposite may have potential applications in solar energy and photovoltaic devices. The red-shift in the absorption edge and direct band gap decrease is directly associated with crystallization of the amorphous Sb$_2$S$_3$ phase$^{3}$. The amorphous Sb$_2$S$_3$/HNTs can be considered as a degenerate direct band gap semiconductor due to the high density of defects and the existence of a large number of states within the energy gap. This was consistent with a plot of $(\alpha h \nu)^{2}$ vs. $h \nu$ (where $\alpha$ is the optical absorption coefficient) for the amorphous as-synthesized sample (Supplementary Fig. S5b), which showed an exponential-like tailing of the straight line; that is, the absorption decreased slowly compared to the crystalline calcined Sb$_2$S$_3$ material below the optical gap. To determine the valence band (VB) and conduction band (CB) positions of the samples, we theoretically calculated the band edge positions of the materials using the atomic electronegativities of the constituent atoms$^{30,31}$. The calculated $E_{VB}$ of the calcined Sb$_2$S$_3$/HNTs was 1.97 eV, similar to that of pure Sb$_2$S$_3$ ($E_{VB} = 1.98$ eV), suggesting that it would also be an potential excellent visible-light responsive photocatalyst in the environmental fields. Laser confocal scanning microscopy was used to record the fluorescence spectra of different samples. As expected, the fluorescence intensities in the presence of Sb$_2$S$_3$ were much higher than the native HNTs with the as-synthesized Sb$_2$S$_3$/HNTs nanocomposites exhibiting higher fluorescence intensities than control samples.
of amorphous Sb$_2$S$_3$ (Supplementary Fig. S6). Although morpho-
logical factors, quantum effects and coupling can influence the fluo-
rescence intensity$^{32}$, the uniform distribution of Sb$_2$S$_3$ nanoparticles
on the surface of the HNTs might be responsible for the higher
intensity by allowing increased numbers of electron and holes to
return to the ground state via optically radiative recombination
routes.

We simulated a surface structure model of amorphous silica by
using crystalline approximations (Supplementary Fig. S7)$^{33}$, and con-
structed the thiol-functionalized silica surface of the native HNTs by
replacing the surface hydroxyl groups of amorphous silica with
mercaptopropyl groups (Fig. 3a–c). Density functional theory
(DFT) calculations gave an average Si–O bond length of 1.60 Å
(Supplementary Fig. S8b). Whilst there were two distinct Si–O bonds
with slightly different bond lengths in the bulk silica crystal, the Si–O
bond lengths were all very close to 1.60 Å after full relaxation of
the whole slab, consistent with the amorphous structure$^{34}$. The
average bond lengths of C–C, C–S and S–H in the covalently linked
–(CH$_2$)$_3$SH surface group were calculated to be 1.517, 1.812 and
1.356 Å (Supplementary Fig. S8d–f), respectively, which agreed well
with previous experimental results (1.524, 1.808, 1.340 Å)$^{35,36}$. More-
over, hydroxyl groups positioned at the base of the surface layer

Figure 3 | Geometric structure and electronic properties of thiol-functionalized silica surface. (a) Side view and (b) top view showing
mercaptopropyl groups. (c) Single Si–(CH$_2$)$_3$SH chain showing bond distances in Å. (d) Total density of states (DOS) and atom-projected density of
states (PDOS) for the silica surface of HNTs covalently functionalized with pendent mercaptopropyl groups. (e) Partial charge density of the HNT
surface, corresponding to the band above the valence band maximum (VBM). The isosurface levels are 0.01 e Å$^3$. 
were in an approximately parallel conformation (Fig. 3a), facilitating the formation of surface hydrogen bonds between nearest neighboring hydroxyls. In contrast, the top of the mercaptopropyl-functionalized silica surface consisted of a diverse distribution of thiol groups due to the abundant lone pairs on the sulfur atoms. In order to gain deeper insight into the strong influence of the mercaptopropyl groups on the in situ surface environment, we performed a dynamic analysis of the HNTs surface structure. Significantly, the bond length distributions in the \((\text{CH}_2)_3\text{SH}\) moiety after 5 ps dynamic equilibrium (Supplementary Fig. S9) demonstrated that the pendant \(-\text{C}_3\text{H}_6\text{SH}\) group altered the SiNTs surface to a rather flexible and variable organic surface, showing a heterogeneous surface structure of covalently linked pendant mercaptopropyl groups.

The valence bands associated with the unfunctionalized silica surface consisted of O 2p states, while the conduction bands were formed from a mixture of O 2s, H 1s, and Si 3s states (Supplementary Fig. S7c). Calculation of the density of states (DOS) and partial charge density for the mercaptopropyl-functionalized silica surface of the HNTs indicated that the lower and upper valence bands were composed of mainly O 2s or O 2p, respectively, along with states hybridized with the \(-\text{CH}_2\text{SH}\) group (Fig. 3d, e). The conduction band near the conduction band maximum (CBM) was mainly a H 1s state, partly hybridized with S 3p states. The most significant change associated with surface attachment of the mercaptopropyl groups was that the lone pair on the S atom introduced a localized band above the valence band maximum (VBM) of pure silica, which contained some states consisting of mixtures of S 3p with C 2p and H 1s states. This was clearly shown in the partial charge density of the HNTs surface (Fig. 3d). Interestingly, the band gap reduced to a value of 3.75 eV, indicating that the HNTs should show a much stronger UV light absorption and chemical reactivity than the pure silica surface.

Given the above FTIR spectroscopic and XPS investigations, we investigated the formation of S–Sb interfacial binding through molecular simulation methods. Previously, it has been reported that a fully hydrogenated silica surface was inert with respect to the adsorption of Au atoms, even though the binding energy between Au and Si surface dangling bonds (3.8 eV) or O dangling bonds (2.7 eV) was higher than that between Au and any surface site at the TiO\(_2\) surface\(^6\). Since the bonding nature is still confusing\(^6\), based on previous research on the adsorption of thiols on Au surfaces\(^6\), we performed DFT calculations for the interfacial binding between Sb\(_2\)S\(_3\) nanoparticles and the deprotonated HNTs surface. The DOS for the Sb\(_2\)S\(_3\)/HNTs nanocomposites surface structure remained the same as the algebraic sum of the DOS of Sb\(_2\)S\(_3\) and that of the HNTs surface before and after physisorption. However, similar to bond formation between Au and \(-\text{SH}\)\(^6\), chemisorption leads to covalent bond formation at the interface to produce a significant change in the electronic structure for the nanocomposites that resulted from electron-stimulated hydrogen desorption (The detailed DOS for the three samples are given in Supplementary Fig. S10). The DOS of the Sb\(_2\)S\(_3\)/HNTs nanocomposites near the Fermi energy was greatly affected by the formed S–Sb covalent bond (Fig. 4). It was observed that the band gap of the nanocomposites was dependent on the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO–LUMO) gap of the assembled Sb\(_2\)S\(_3\) nanoparticles in region I, indicating that the highest optical adsorption wavelength should not be obviously changed after chemisorption. However, the rather localized mixed states of Sb\(_2\)S\(_3\) and the HNTs overlap in region II, and the mixed charge density in region III demonstrates that significant electronic structure changes occur upon the formation of S–Sb covalent bonds during the adsorption process.

Fig. 5 shows the calculated charge density difference at the Sb\(_2\)S\(_3\)/HNTs interface. Charge transfer was particularly noticeable at the Sb–S bond traversing the interface between Sb atoms of the Sb\(_2\)S\(_3\) nanoparticle and S atoms of the thiol moiety on the HNT surface (see dotted circles in Fig. 5b). The Mulliken charges on the Sb and S atoms in the Sb\(_2\)S\(_3\) nanoparticles ranged from 0.41 to 0.66 e, and \(-0.37\) to \(-0.56\) e, respectively, which as expected were considerably less than values for the bulk structures due to the decreased coordination numbers associated with atoms in nanoscale clusters or at surface sites. With regard to the HNTs template, the Mulliken charges of the S atoms ranged from \(-0.11\) to \(-0.14\) e, corresponding to the observed by XPS data that showed a higher binding energy (162.10 eV) of S 2p compared to that of the S atoms (161.58 eV) in Sb\(_2\)S\(_3\). The charges of Sb, S, C at the relaxed nanocomposite interface were 0.93 e, \(-0.22\) e, 0.61 e, respectively (Fig. 5b), which were different from the charges of 0.63 e, \(-0.15\) e, 0.64 e before chemisorption, indicating significant charge transfer at the Sb\(_2\)S\(_3\)/HNTs interface. These theoretical calculations coincided well with the experimental results, revealing the origin of the interfacial affinity of the mercaptopropyl functional groups for the Sb\(_2\)S\(_3\) nanoparticles and their strong aggregation onto the outer surface of the HNTs.

Figure 5 | Interface between Sb\(_2\)S\(_3\) nanoparticles and HNTs. (a) Side (upper panel) and top (lower panel) view of the interface between Sb\(_2\)S\(_3\) nanoparticles and the mercaptopropyl-functionalized silica surface of a HNT in Sb\(_2\)S\(_3\)/HNT nanocomposites. (b) Charge density difference of the Sb\(_2\)S\(_3\)/HNT interface plotted along the plane designated by the dotted lines shown in the lower panel of (a). Blue corresponds to charge depletion and red to charge gain. Isosurfaces are shown in the range \([\pm 0.05, 0.05]\) (e/Å\(^3\)). Contours of constant charge density are separated by 0.003 eV/Å\(^3\). The small yellow or violet balls represent S or Sb atoms, respectively, in Sb\(_2\)S\(_3\) nanoparticles. The large yellow, black, or white balls represent S, C, or H atoms in the HNT surface.
Although a similar mode of charge transfer was determined for the interfaces between thiol groups and Au or Ag atoms\(^{20,41-43}\), the details of the mechanism remains obscure. We hope our results therefore provide both specific and general insights into the nature of interfacial interactions in multi-component nanomaterials with integrated structure and function.

**Discussion**

As for the synthesis of \(\text{Sb}_2\text{S}_3/\text{HNTs}\), we also investigated the influence of the \(\text{Sb}:\text{Si}\) molar ratio, as well as the effect of the order of addition of the reactants, on the fidelity of the templating process. No significant modifications in the as-synthesized or calcined materials were observed when the \(\text{Sb}:\text{Si}\) molar ratio was changed from 1:1 to 1:10, which corresponded to \(\text{Sb}_2\text{S}_3\) silica mass ratios ranging from 17.6 to 17.60, respectively, in the hybrid materials. However, at \(\text{Sb}:\text{Si} = 1:10\), the relatively low \(\text{Sb}\) content resulted in sporadic deposition of \(\text{Sb}_2\text{S}_3\) nanoparticles across the surface of the silicified polymer tubules rather than a uniform distribution (Supplementary Fig. S11a, b and S12). Under these conditions, the reduced rate of inorganic nucleation was also associated with an approximate two-fold increase in the mean size of the individual \(\text{Sb}_2\text{S}_3\) nanoparticles to a value of 15.6 nm. Interestingly, replacing the simultaneous addition of TAA and HNTs to the antimony chloride solution with a procedure in which TAA was added first, followed by an aliquot of the HNTs suspension only after the reaction solution had turned orange in color, also produced silicified polymer myelin tubules coated with uniform-sized \(\text{Sb}_2\text{S}_3\) nanoparticles, 11.0 nm in mean size (Supplementary Fig. S11c). Although we could not rule out the possibility of primary nucleation occurring directly on the surface of the nanotubular template, our results suggested that formation of \(\text{Sb}_2\text{S}_3\) nanoparticles in solution followed by strong adsorption onto the surface of the thiol-functionalized silica-coated polymer nanotubes was the principal mechanism underlying the surface decoration process. Our results also indicate that non-equilibrium processes of \(\text{E}_1\text{B}_2\text{S}_2\) myelination can be used to prepare thiol-functionalized, polymer/silica HNTs with high shape anisotropy, which in turn can be exploited as nanostructured templates for the controlled spatial deposition of amorphous \(\text{Sb}_2\text{S}_3\) and its subsequent transformation to silica embedded with crystalline \(\text{Sb}_2\text{S}_3\) nanoparticles.

In summary, the uniform \(\text{Sb}_2\text{S}_3\) nanoparticles were spontaneously assembled as packed arrays on thiol-functionalized silica/polymer myelin-like nanotubular templates to produce novel hybrid multi-functional nanocomposites. A theoretical prototype of a hybrid myelin-like nanotubular templates to produce novel hybrid multi-assembled as packed arrays on thiol-functionalized silica/polymer platforms for the synthesis and assembly of nanoparticles to produce nanostructured tubules with tailored and enhanced functional properties. Furthermore, the electronic structure information derived from DFT calculations reported herein could potentially achieve the full atomic-level analysis of hybrid nanocomposites in general.

**Methods**

**Materials synthesis.** Hybrid nanotubes of thiol-functionalized silica–E\(_1\)B\(_2\)S\(_3\) myelin-like nanotubular surface structure were proposed, and DFT calculations of the geometric structure and the electronic properties of the SiO\(_2\) (particle) component were considered in the calculation of the relaxed bulk structures, we adopted the original cell parameters for the following calculations. The slab thickness of silica was varied from 1 to 10 monolayers, which in turn can be exploited as nanostructured templates for the controlled spatial deposition of amorphous \(\text{Sb}_2\text{S}_3\) and its subsequent transformation to silica embedded with crystalline \(\text{Sb}_2\text{S}_3\) nanoparticles.

In summary, the uniform \(\text{Sb}_2\text{S}_3\) nanoparticles were spontaneously assembled as packed arrays on thiol-functionalized silica/polymer myelin-like nanotubular templates to produce novel hybrid multi-functional nanocomposites. A theoretical prototype of a hybrid myelin-like nanotubular templates to produce novel hybrid multi-assembled as packed arrays on thiol-functionalized silica/polymer platforms for the synthesis and assembly of nanoparticles to produce nanostructured tubules with tailored and enhanced functional properties. Furthermore, the electronic structure information derived from DFT calculations reported herein could potentially achieve the full atomic-level analysis of hybrid nanocomposites in general.
Furthermore, we employed a HNT model surface structure with the surface –OH groups replaced by –(CH$_2$)$_3$SH moieties, giving a total of 216 atoms. The slabs were separated by a vacuum region of 25 Å along the perpendicular direction. The geometric and electronic properties were analyzed using both hydrated and dehydrated models before further investigations of the interface mechanism operating between the assembled nanoparticles and the HNTs substrate. The interfacial model comprising suitable structures was then considered an appropriate theoretical description to elucidate the experimental observations.

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