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Surfactant-Assisted Synthesis of SnS Nanowires Grown on Tin Foils

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ABSTRACT: Crystalline SnS wires of micro- and nanometer scale have been synthesized over tin metal foils at room temperature using a simple surfactant-assisted approach. Scanning electron microscopy, transmission electron microscopy, UV–Vis–near infrared (NIR) and Fourier transform infrared (FTIR) spectroscopy were used to characterize the SnS nanowires. X-ray diffraction (XRD) analysis confirmed the formation of the pure orthorhombic phase of SnS. The optical band gap of the samples was found to be ~ 1.4 eV. From the investigation, the formation of nanowires could be explained in two steps: initial cracking/splitting of the nanoflakes was followed by a top-growth mechanism to form ultralong nanowires. Effects of various experimental parameters on the growth mechanism were investigated. Present studies have shown that this facile process also can be extended for the synthesis of other low dimensional structures.

Introduction

During the past few decades, much effort has been focused on designing novel methods to prepare semiconductor metal chalcogenide nanomaterials owing to their potential applications in electronic and optical devices.^{1–4} One-dimensional (1D) nanostructures are of particular interest because of their fundamental importance and wide range of potential applications in nanodevices.^{3,4} Vapor–liquid–solid (VLS) growth, chemical vapor deposition (CVD), and template-assisted approaches have been developed to prepare 1D nanostructured metal chalcogenide semiconductors, but in most of the cases the product was in powder form. Now, fabricating the nanostructures, modifying their morphologies, and measuring their properties are the challenges faced by material scientists. In this respect, the oriented growth of 1D nanomaterials on substrates is considered to be a definitive step toward the fabrication of advanced electronic and optoelectronic nanodevices.⁵ It has long been established that surfactant molecules which are useful as versatile soft templates can form different conformations by self-assembly and lead to the formation of different nanostructures.^{6,7} By taking advantage of these fascinating structures, designing of the different nanoscale quantum devices becomes feasible.

Tin sulfide is one of the most important compounds showing a variety of phases, such as SnS, SnS₂, Sn₂S₃, and Sn₃S₄ due to the versatile coordinating characteristics of tin and sulfur. Tin monosulfide (SnS) is an important IV–VI group semiconductor material with a band gap of 1.33 eV.⁸ It belongs to the group of layered semiconductors having orthorhombic structure, where the Sn and S atoms are tightly bonded in a layer and the layers are bonded by weak van der Waals forces.⁹ In particular, SnS has attracted researchers owing to its interesting properties and potential application in photoconductors,¹⁰ near-infrared detector,¹¹ holographic recording systems,¹² and photovoltaic materials with high conversion efficiency.^{13,14}

There are few reports on the synthesis of different metal sulfide and oxide nanostructures directly on the corresponding metal foils by different techniques.^{5,15–20} Gas–solid reaction has been proven to be a useful approach as it can be carried out at a low temperature, and it is also cost-effective. Yang et al.^{17,18} synthesized Cu₂S nanowires with good crystallinity and

a large aspect ratio by exposing a surfactant-treated copper surface to H₂S at room temperature. In this article, we demonstrate a facile surfactant-assisted gas–solid reaction approach to grow micro- and nanowires of tin sulfide on the tin metal surface at room temperature. This method is a versatile one as it directly facilitates device fabrication and characterization, and it is also simple and cost effective. In this paper, a possible explanation for the formation of nanowires has been suggested.

Experimental Section

SnS nanowires were prepared on the surface of tin foils in the following way. The surface of the foil was cleaned with water and ethanol and then heated at 100 °C for 20 min. Then the foil was dipped into an aqueous solution of the cationic surfactant cetyltrimethylammonium bromide (CTAB). The surfactant concentration was maintained at 6.9×10^{-2} M. The foils treated with surfactants were transferred to a closed vessel and were exposed to a static H₂S atmosphere for 12 h at a constant pressure of ~ 1.1 atm. The H₂S gas was prepared from the reaction of aqueous solution of Na₂S and HCl. After a few minutes, the surfactant-covered tin foil surfaces became grayish black indicating the formation of SnS.

The crystalline phases of the products were determined by X-ray powder diffraction (XRPD) by a Seifert 3000P diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å). The morphologies of the samples were studied by a scanning electron microscope (SEM; Hitachi S-2300) at an accelerating voltage of 25 kV. Microstructural and crystal structures were obtained using a high-resolution transmission electron microscope (HRTEM; JEOL 2010). For transmission electron microscopy (TEM) measurements, the foil surface was carefully scratched out and the black mass obtained was dispersed in isopropyl alcohol. From the solution, few drops were deposited on a carbon coated copper grid. The purity and composition of the prepared samples were studied by energy-dispersive X-ray analysis (EDAX) (Oxford instruments, INCAx-sight) attached with TEM. Fourier transform infrared (FTIR) spectra of the samples were recorded in the wavenumber range of 4000 to 400⁻¹ cm with a Shimadzu model 84005 FTIR spectrometer using a KBr wafer. Optical transmittance spectra of the samples were recorded with a UV–Vis–near infrared (NIR) spectrophotometer (Hitachi, U-3410).

Results and Discussion

Figure 1a shows the X-ray diffraction (XRD) pattern of a representative Sn foil used as the precursor material. In the XRD patterns of the samples prepared with and without CTAB (Figure 1, panels c and b, respectively), except reflections of Sn metal (marked as *), all the diffraction peaks can be indexed to the

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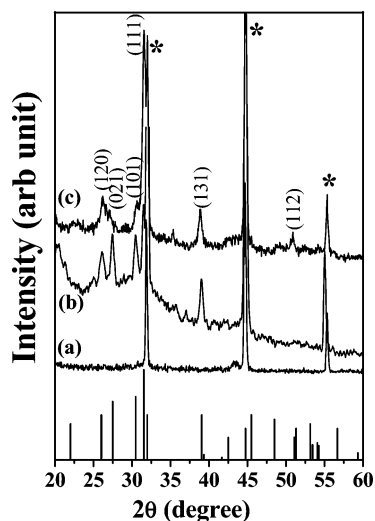


Figure 1. XRD patterns of (a) Sn foil, (b) SnS nanoflakes without using CTAB, and (c) SnS nanowires using CTAB. Asterisks indicates peaks of metallic tin, and the bottom bars show the standard SnS from JCPDS Card No. 39-0354.

pure orthorhombic phase of SnS. The cell constants were calculated to be from Figure 1b: $a = 4.3222 \text{ \AA}$, $b = 11.161 \text{ \AA}$ and $c = 3.9929 \text{ \AA}$ and from Figure 1c: $a = 4.2649 \text{ \AA}$, $b = 11.0843 \text{ \AA}$, and $c = 4.0187 \text{ \AA}$, respectively. The values are comparable with the standard values ($a = 4.3291 \text{ \AA}$, $b = 11.1923 \text{ \AA}$ and $c = 3.9838 \text{ \AA}$) reported in the literature (JCPDS Card No. 39-0354).

The purity and composition of the prepared samples were determined by energy-dispersive X-ray analysis (EDAX). The EDAX spectrum of the nanowires prepared using CTAB is shown in Figure 2a, which indicates that the atomic ratio of Sn to S is 1.2: 1; showing the phase of the obtained product as SnS. A little excess of Sn fraction is probably due to the contribution from Sn foil substrate. The carbon peak may be due to presence of CTAB over the nanowires or may be from the carbon coating on the copper grid. The presence of oxygen peak may be due to surface oxidation of the nanowires at the time of ultrasonication for preparing the TEM grid.

To confirm the presence of the surfactant on the nanowires, FTIR spectroscopy of the products was performed in the range 4000 to 400 cm^{-1} . FTIR spectra of (i) pristine CTAB and (ii) SnS nanowires are shown in Figure 2b. For pristine CTAB, the spectrum shows two intense bands at 2918 and 2850 cm^{-1} , assigned to asymmetric and symmetric stretching vibrations of C—CH₂ in the methylene chains.²¹ These bands with less intensity are also present in Figure 2b (ii). This indicates that the surfactant is present on the synthesized tin sulfide nanowires. The broad band between 3200 and 3600 cm^{-1} and the band centered at 1622 cm^{-1} in the spectra were assigned to O—H stretching and deformation vibrations of weak-bound water molecules in the materials.²¹

The morphologies of the samples were studied by SEM, which are shown in Figure 3a–e. The figures elucidate the way; the SnS nanowires grew from the rough tin surface using CTAB as the template. It was observed that the growth of the nanowires was directly from the metal surface, which has been shown by a dotted circle in Figure 3a. The higher magnification image (Figure 3b) shows that the nanowires were very long (length 5–20 μm) with diameters within 100–200 nm. Figure 3c shows the initiation of the nanowires from the metal surface, when the reaction was carried out for 30 min. From the figure it can be well observed that the base of the nanowire is very wide

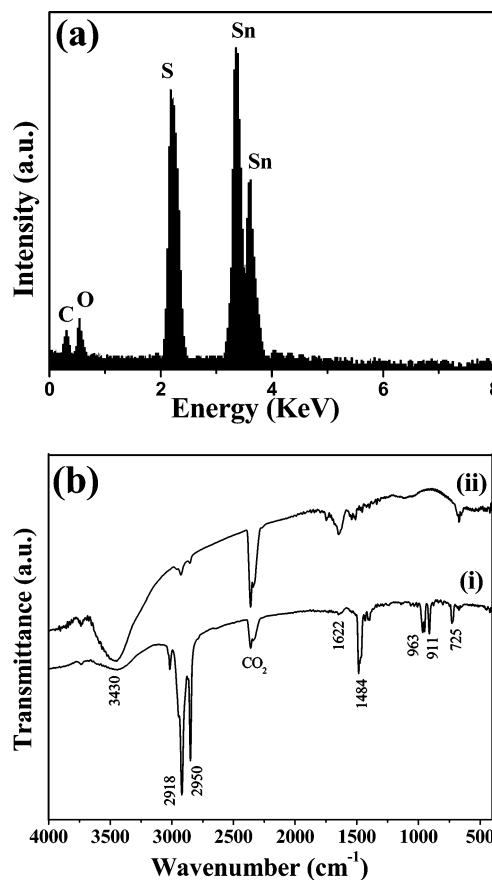


Figure 2. (a) EDAX spectrum of SnS nanowires and (b) FTIR spectra of (i) pure CTAB and (ii) the prepared SnS nanowires.

similar to the flakes. After a long exposure to H₂S, the nanowires developed from the flakelike structures in the presence of surfactant, probably through splitting of the flaky structures, which is clearly shown in Figure 3d. The arrow marks in Figure 3d indicate the flakelike base, which split into the nanowires on the metal surface. The surfactant treatment on the foil surface and oxidation of the metal foil were found to be the key steps for the growth of the nanowires. To investigate the effects of surfactants on the structure and morphology of the product, contrastive experiments were conducted. When the experiment was carried out in the absence of CTAB, the resulting products were only nanoflakes of $\sim 100 \text{ nm}$ width, as shown in Figure 3e. However, no nanowires or flakes were formed by passing dry H₂S gas (H₂O was absorbed by passing through anhydrous CaCl₂) even in the presence of surfactant. This indicates that the water molecules present inside the reaction vessel also play an equally important role in the growth of the nanowires. To verify the effect of oxidation, the foils were treated with HCl vapors for few minutes and then dried in air. From the XRD data (see Supporting Information) it was observed that a thin SnO layer was formed over the metal foil. The foil was then treated with the surfactant solution, and sulfurization was carried out inside the reaction vessel. It was observed that very long nanowires that were dense in quantity formed over the foil (see Supporting Information). If the reaction vessel was initially deaerated with N₂, without changing the other experimental conditions, the tin sulfide nanostructures could not be obtained on the tin foil surface. This suggests that O₂ present inside the vessel is required for the formation of the oxide layer over the foil.

A more detailed study on the crystal structure of the nanowires was performed by TEM analysis. Figure 3f shows

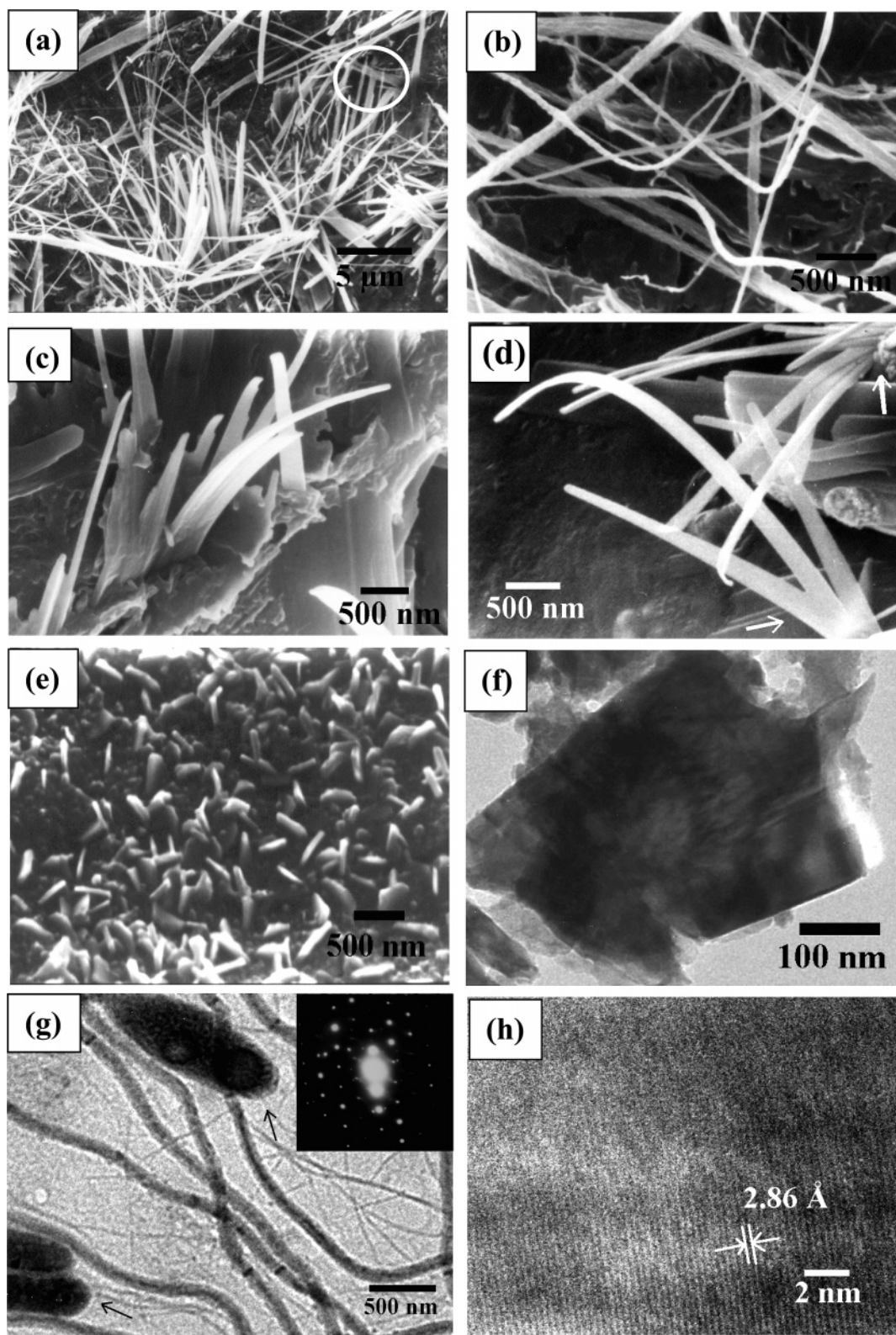


Figure 3. SEM images of (a) SnS nanowires, (b) higher magnification of the nanowires, (c) image showing the initiation of the nanowires from the metal surface after a 30 min exposure to H_2S , (d) formation of nanowires from nanoflakes and (e) SnS nanoflakes over the metal foil without using CTAB. TEM bright field images of (f) a nanoflake formed after 30 min of reaction, (g) nanowires and the inset is the SAED pattern of a nanowire and (h) the HRTEM image of a nanowire showing lattice fringes.

the low resolution TEM image of a nanoflake formed at an intermediate stage after 30 min exposure to H_2S . Nanowires were formed by lateral splitting of this type of nanoflake. Figure 3g indicates the nanowires formed when the reaction was allowed for 12 h. The arrow marks in the figure indicate the flakelike

base of the nanowires. From the figure, it was observed that the nanowires were very long with a diameter of ~ 120 nm. The inset in Figure 3g is the selected area electron diffraction (SAED) pattern of a nanowire, indicating the single crystalline nature of the SnS nanowires. Figure 3h shows the HRTEM

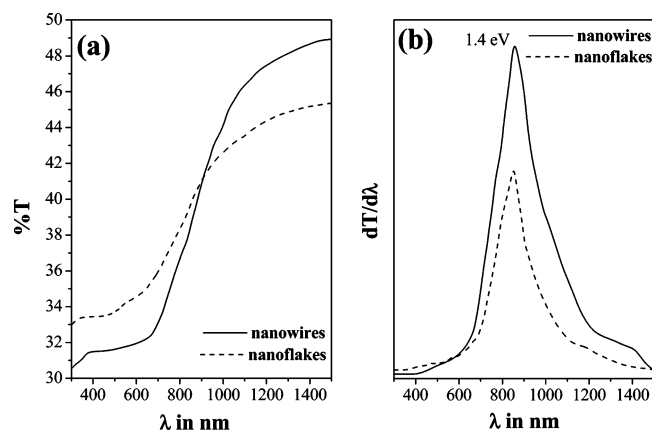


Figure 4. (a) Transmittance (%*T*) vs wavelength (λ) plot of the SnS nanowires and nanoflakes and (b) differential transmittance spectra of SnS nanowires and nanoflakes.

image of a nanowire with lattice fringe spacing of 2.86 Å, corresponding to the (111) lattice planes of the orthorhombic SnS.

Figure 4a shows the optical transmittance (%*T*) vs wavelength (λ) plot of the samples prepared with and without using CTAB in the range of 300–1500 nm. To record the optical spectra, the foils were scratched out and dispersed homogeneously in isopropyl alcohol. The band gaps of the materials were determined from the differential spectra^{19,22} of the samples, which are shown in Figure 4b. The band gap of the nanoflakes (prepared without CTAB) and nanowires is ~ 1.4 eV, which is comparable with the reported bulk value.⁸

From the above investigations, the growth process of the nanowires can be explained in two steps: (i) the cracking of the nanoflakes to nanowires and (ii) further elongation of the split flake parts to form ultralong nanowires. In the process, we supplied the as-prepared moisturized H_2S gas to the reaction vessel, where an excess of HCl was used in the preparation of the gas. This makes the environment acidic, which initially favors the oxidation of the metal foil surface to form a thin SnO layer over it by reacting with the O_2 present inside the vessel. From the oxide surface, Sn^{2+} ions were generated through the reaction of SnO and HCl, and hence a continuous supply of Sn^{2+} ions from the metal oxide surface was facilitated,²³ which react with H_2S to form SnS. Controlled experiments were carried out in which the prepared H_2S gas was bubbled through water before passing to the reaction vessel to remove the HCl vapor. In this case, no SnS nanostructures were formed. When H_2SO_4 was used in place of HCl, without changing the other experimental conditions, tin sulfide nanostructures could not be obtained on the metal foil surface. These experiments suggested that the HCl vapor accompanied with H_2S gas inside the vessel is necessary for formation of SnS nanostructures. At the initial stage, constant exposure to H_2S favors the growth of SnS nanoflakes because of its intrinsic anisotropic nature. In SnS, each tin atom is coordinated by six sulfurs in a highly distorted octahedral geometry. As the octahedra are so distorted the tin atom is actually displaced toward one of the faces of the octahedra. This leads to three short Sn–S bonds of ~ 2.7 Å and three long Sn–S bonds of almost ~ 3.4 Å. There are two SnS layers in one unit cell, and one of the long distance sulfurs actually resides on the neighboring SnS layer. This weak Sn–S interaction binds the two tin sulfide layers together to form a double-layer structure perpendicular to the *c*-axis. The weak van der Waals forces between these layers provide the possibility of formation of this

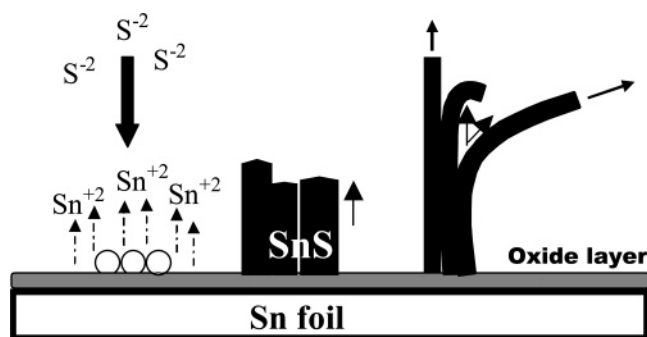


Figure 5. Schematic model showing different stages for the growth of SnS nanowires on the tin metal foil.

type of structure.^{24,25} With an increase in the duration of exposure to H_2S atmosphere, due to the inherent asymmetry of the layered SnS structures, the intrinsic tension prevails in the crystal structure, causing the rolling up of the edges of the sheets/flakes. Finally, the tension is released by the cracking of the flakes into nanowires.^{26,27} Such initiation of furcation of flakes is clearly shown in Figure 3c,d, which supports the aforesaid mechanism. A similar hydration–exfoliation–splitting model also has been proposed by other workers to explain the formation of nanowires from the cracking of nanoflakes.^{28,29} Then the further elongation of the nanowires can be explained on the basis of the top-growth mechanism proposed by Yang et al.^{17,18,30} The hydrophilic group of surfactant layer might passivate the surface of the SnS nanowires³¹ and restrict the lateral growth. The water molecules provided by the moist H_2S serve as an atomic transport layer along the nanowire surface, through which the Sn^{2+} ions move from the bottom to the top of the nanowire and react with H_2S to form SnS. Figure 5 highlights the formation steps of the nanowires on the foil surface.

Conclusion

At room temperature, crystalline SnS nanowires were successfully prepared over tin metal foils by using a simple surfactant-assisted approach. From XRD and TEM analyses, the nanowires were found to be of pure orthorhombic phase of SnS. A plausible flake splitting mechanism followed by a top-growth mechanism has been elucidated for the formation of the nanowires. Considering the simplicity of the procedure used in this SnS nanowire preparation, this surfactant-assisted route seems to be promising, which may be extended to fabricate other metal sulfide nanostructures directly over metal foils.

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Supporting Information Available: XRD spectrum of oxidized tin foil indicating formation of the SnO layer over the metal foil; SEM image of SnS nanowires formed over oxidized tin foil surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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