In Situ Observation of Thermally Induced Structural Transitions in Vacancy-Doped Cuprous Telluride (Cu$_{2-x}$Te) Nanowires Using Raman Spectroscopy

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ABSTRACT: A fundamental understanding of the thermal stability of vacancy-doped cuprous telluride nanocrystals (Cu$_{2-x}$Te NCs) will be conductive to their exploitation in plasmon-related applications. However, the thermally induced structural and Raman spectral changes of Cu$_{2-x}$Te NCs have remained fairly unexplored so far. Here, temperature-induced structural transitions of Cu$_{2-x}$Te nanowires (NWs) are studied by in situ Raman spectroscopy from $-190$ to $530$ °C. Results reveal a dramatic temperature dependence of Raman signatures of Cu$_{2-x}$Te NWs, serving as a potent indicator for their structures and structural transitions. The hexagonal weissite-to-orthorhombic phase transition takes place in the cooling process from $25$ °C to $-190$ °C. An intermediate state of high degree of disorder with featureless Raman spectra is observed before its dissociation into the elemental Cu and the high-temperature phase above $480$ °C. This work provides fundamental insights into the thermally induced structural stability of Cu$_{2-x}$Te NWs and will further stimulate new exploration of their plasmon-related practical applications.

INTRODUCTION

Vacancy-doped cuprous telluride nanocrystals (Cu$_{2-x}$Te NCs) represent an emerging class of promising semiconducting plasmonic materials for a plethora of potential exploitations in photovoltaics,3−7 photonics,3 thermoelectric energy conversion,1,2 photonothermal cancer therapy,7,8 unlike traditional plasmonic noble metals (i.e., Au, Ag), fantastic plasmonic properties originating from the collective oscillation of free holes in the valence band of copper-deficient Cu$_{2-x}$Te are responsible for these applications.9,7 The low carrier (hole) concentration of $\sim 10^{19}−10^{21}$ cm$^{-3}$ in Cu$_{2-x}$Te NCs yields a plasmon resonance band that is tunable in the near-infrared region, which offers high tissue penetration depth favorable for in vivo optical imaging and spectroscopic detection.9,7 In the past several years, intensive efforts have been devoted to the controllable synthesis of Cu$_{2-x}$Te NCs over size, shape, and composition and thereby for the tuning of their plasmonic properties.9,10 It is widely recognized that the Cu$-$Te phase diagram is the most complex one with different crystal phases and structures dependent on the relative stoichiometry.9,10 Mild changes in external settings (i.e., temperature, pressure, chemical reagents) could greatly affect the crystal structures and compositions of Cu$_{2-x}$Te NCs; a subtle compositional modification could lead to significant changes in their crystal structures and thereby plasmonic behaviors. All these changes could cause variations of the performance of devices for a diversity of applications based on Cu$_{2-x}$Te NCs to some extent.

The stoichiometric Cu$_2$Te is intrinsically unstable under ambient conditions and rapidly degrades into its Cu-deficient Cu$_{2-x}$Te phases.3,11,12 Cu$_{2-x}$Te can exist in a diversity of structural forms, specifically including Cu$_2$Te (weissite, hexagonal), Cu$_x$Te$_2$ (trigonal), Cu$_x$Te$_y$ or Cu$_y$Te$_2$ (nickardite, tetragonal), Cu$_x$Te (vulcanite, orthorhombic), and Cu$_x$Te$_2$ or Cu$_x$Te$_y$ (pyrite, hexagonal).3 In all of these crystal structures, the Cu atoms are unusually mobile within the closed-packed Te framework, with its arrangement depending on the stoichiometry. With the temperature increase from room temperature to above 500 °C, Cu$_{2-x}$Te could undergo successive phase transitions generally described as α phase $\rightarrow$ 275 °C β phase $\rightarrow$ 320 °C γ phase $\rightarrow$ 365 °C δ phase.13,14 The high-temperature δ phase is the normal phase, which upon cooling below 365 °C transforms into the incommensurate β and γ phases and finally to the commensurate α phase below 275 °C. Recent studies observed Cu precipitation during the transition of the stoichiometric Cu$_2$Te into the Cu-deficient Cu$_{2-x}$Te at high temperatures.15 The theoretical calculations showed that the transition heat was as low as $\sim 1.4$ kJ/mol at 69 591 °C or $\sim 2.81$ kJ/mol at 360 °C.15,16 In addition, the first- principles calculations also demonstrated the structural transitions of Cu$_{2-x}$Te from monoclinic (when $x = 0$) to trigonal (0.125 $\leq x \leq 0.625$) and hexagonal (0.75 $\leq x \leq 1$), along with the Cu precipitation.16 Thus, the complexity and thermal instability of the crystal structures of Cu$_{2-x}$Te make a
The complete understanding of their structures and plasmonic properties greatly challenging. Variations of thermal conductivity and thermoelectric performance of Cu$_2$Te with the temperature were previously observed in the temperature range from 25 to >1000 °C, attributed to the temperature-induced structural changes. $^{1,8}$ Cu$_2$Te has been extensively employed as the back contact layer material in the CdTe solar cells, which can enhance the optical transmission in the near-infrared region and promote the photoelectric conversion efficiency of solar cells. $^7$ However, it was recently found that the high-temperature processing of the devices at temperatures of 100–400 °C degraded the solar cell device performance due to the temperature-induced structural changes. $^{1,8}$ Most of the previous studies mainly performed the structure characterization for Cu$_2$Te materials and its devices in an ex situ manner, which might not reflect the real composition and structures existing in practical applications due to the difference between in situ and ex situ settings. In addition, Cu$_2$Te may undergo the pre- or post-processing under robust environments (i.e., high pressure and low or high temperatures) for the fabrication of biomedical devices or high-power laser irradiation for photothermal and photodynamic therapy. $^{7,18}$ These treatment processes may induce changes of Cu$_2$Te structures and thus optical properties of Cu$_2$Te-based applications.

Therefore, a full understanding of the temperature-induced structural changes in a broad temperature range of Cu$_2$Te is critical and would definitely benefit the design of high-performance devices based on Cu$_2$Te with long-term stability.

The X-ray diffraction (XRD) technique has been widely documented to study the structural changes of Cu$_2$Te NCs at distinct temperatures, but strong evidence showed that Cu$_2$Te of distinguishable electronic and crystal structures possessed similar XRD patterns. $^{13,14,19,20}$ Subtle differences among XRD patterns of Cu$_2$Te with different crystal structures compromise the XRD techniques for the determination of crystal phases of Cu$_2$Te. This also complicates the investigations of structural transitions of Cu$_2$Te NCs in varied settings. In addition, the phase transitions of Cu$_2$Te were also examined by both differential thermal analysis (DTA) and electron diffraction methods, which showed a series of phase transition temperatures and the temperature-dependent evolutions of electron diffraction patterns featuring their crystal structures, respectively. $^{13,14,19}$ However, all of these studies were only carried out at high temperatures beyond room temperature. Raman spectroscopy has emerged as a nondestructive, highly sensitive spectroscopic technique for the structural analysis with chemical signatures. $^{21–28}$ In situ Raman spectroscopy could provide direct insights into the structural changes within a local domain of Cu$_2$Te with the spectral evolution of their Raman signatures. In this work, upon combining in situ Raman spectroscopy with in situ XRD measurements, we addressed the following critical issues remaining unanswered in Cu$_2$Te nanowires (NWs): (i) evolution of Raman spectral profiles with the temperature, (ii) correlations of the Raman spectral signatures with the structural changes of Cu$_2$Te NWs at varied temperatures, and (iii) the structural evolution of Cu$_2$Te NWs over a broad temperature range from the cryogenic temperatures (−180 °C) to high temperatures. We found a dramatic temperature...
dependence of Raman features of Cu$_{2-x}$Te NWs during the cooling–heating process (25 °C → −190 °C → 25 °C → 530 °C). Raman signatures can serve as a potent indicator for the crystal structures and structural changes of Cu$_{2-x}$Te NWs. Our work provides useful information on the temperature-dependent structural stability of Cu$_{2-x}$Te NWs over a broad temperature range and would strengthen the understanding of both structure- and composition-dependent optical properties for plasmon-related applications, potentially benefiting the design of high-performance devices for a diversity of applications.

RESULTS AND DISCUSSION

The Cu$_{2-x}$Te NWs were synthesized by a two-step process, as shown in Figure 1A.\textsuperscript{29,30} Te NWs were first synthesized using a hydrothermal method by reduction of sodium telluride at 180 °C with hydrazine hydrate in the presence of both ammonium hydroxide and poly(vinylpyrrolidone) (PVP). Then, the resultant Te NWs serve as the sacrificial template and were reacted with the Cu$^{2+}$ precursor and ascorbic acid (AA) to produce the Cu$_{2-x}$Te NWs. In this synthesis, AA plays a critical role in preventing the elemental Cu production due to its mild reducing power favorable for reducing the Cu$^{2+}$ to Cu$^0$ rather than Cu$^{2+}$;\textsuperscript{31,32} PVP works as the directing agent to facilitate the anisotropic growth of Te, producing Te NWs.\textsuperscript{27} A blue-to-yellow color change was observed with the conversion of Te NWs to Cu$_{2-x}$Te NWs. The Cu to Te atomic ratio was determined to be 1.97 by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Figure S1). The absorption spectrum of Te NWs shows a characteristic band centered at 635 nm, while the broad band at ∼1300 nm in Cu$_{2-x}$Te NWs is attributed to the plasmon resonance absorption supported by the hole carriers (Figure 1B). All diffraction peaks in the XRD pattern of Te NWs can be indexed to the hexagonal structure according to the JCPDS no. 036-1452, and the XRD pattern of Cu$_{2-x}$Te NWs unambiguously substantiated the formation of weissite Cu$_{2-x}$Te (JCPDS no. 010-0421) (Figure 1C).\textsuperscript{33} Both Te NWs and Cu$_{2-x}$Te NWs show no other diffraction peaks in their XRD patterns, indicating their high purity. The Raman spectrum of Te NWs exhibits three sharp Raman bands located at 91, 120, and 139 cm$^{-1}$ that are assigned to the E$_1$ transverse (TO) phonon mode, A$_1$ mode, and E$_2$ mode, respectively (Figure 1D). These Raman features are in good accordance with previous observations of Te nanostructures in the literature.\textsuperscript{25,34} In contrast, Cu$_{2-x}$Te NWs possess a broad spectral feature with weak Raman bands at 68, 77, 116, and 138 cm$^{-1}$ that are assigned to the E$_1$ transverse (TO) phonon mode, A$_1$ mode, and E$_2$ mode, respectively (Figure 1D). These Raman features are in good accordance with previous observations of Te nanostructures in the literature.\textsuperscript{25,34}
temperature hexagonal Cu2Te phase (JCPDS no. 065-3460) to be due to the phase transition of the orthorhombic Cu2Te. Surprisingly, the peaks at 2θ = 43.3° and 50.4° revealed the appearance of the elemental Cu, accompanied by the complete disappearance of the orthorhombic Cu2Te phase when exceeding 480 °C. The preservation of the elemental Cu after cooling back to 25 °C from 530 °C justifies the irreversible phase transition of the orthorhombic Cu2Te into the high-temperature hexagonal Cu2Te phase at 480 °C. We also observed the temperature-induced diffraction angle shift toward the low 2θ angles due to the thermal volume expansion. A dark-to-brown color change took place for the Cu2−xTe NW powder sample after the in situ XRD measurement (Figure 3C). Thus, careful analysis of XRD patterns reveals the temperature-induced structural transitions with subtle changes of these XRD patterns of Cu2−xTe NWs in the temperature range of −190 to 530 °C.

Important information concerning the structural transitions can be obtained with the symmetry variation of the crystal system by Raman spectroscopy. According to the group’s theoretical analysis, the optical phonon modes of hexagonal weissite Cu2−xTe comprise longitudinal (LO) and transversal (TO) phonon modes, and their irreducible representations at the Brillouin-zone center can be described as follows: \( \Gamma = 2A_g + 2B_{2g} + 2B_{3g} + B_{1u} + B_{2u} + B_{3u} \) where only the six TO modes \( (A_g, B_{2g}, \text{and } B_{3g}) \) are Raman active. To implement the in situ Raman measurements, Cu2−xTe NWs were first spin-coated on a cleaned silicon substrate, and then Raman spectra were obtained for both Te NWs and Cu2−xTe NWs (Figure 2). High yield and uniform nanowires can be clearly observed for both Te NWs and Cu2−xTe NWs. The diameters of both Te NWs and Cu2−xTe NWs were 10.6 ± 1.4 nm and 12.7 ± 1.0 nm, respectively, statistically estimated on the basis of their TEM data. The conversion of Te NWs to Cu2−xTe preserves the nanowire morphology but causes a slight increase in the diameters due to the Cu atom incorporation. Therefore, our aforementioned results confirm the successful synthesis of high-quality Cu2−xTe NWs.

At room temperature, the as-prepared Cu2−xTe NWs possess a weissite crystal structure belonging to the hexagonal crystal system \((P6_3/m1 \ (156) \text{ space group})\), as shown in Figure 1C,E. To shed light on the structural transitions of Cu2−xTe NWs, in situ XRD measurement was first performed at temperatures between −190 and 530 °C (Figure 3A). The measurement was started at 25 °C followed by the cooling process to monitor the structural transitions in the low-temperature region (Figure S2). By lowering the temperature below 25 °C, an obvious diffraction peak at 2θ = 25.3° shows up, which is indexed to the (048) plane of the orthorhombic Cu2Te (JCPDS no.: 045-1279). This indicates the partial transition of the hexagonal weissite Cu2−xTe into the orthorhombic Cu2Te, yielding their mixture below 25 °C. The low-temperature orthorhombic Cu2Te phase is still preserved after warming up to 25 °C from the lowest measurement temperature (−190 °C) (Figure 3A,B). However, with the temperature further increasing to above 300 °C, we found the appearance of the high-morphology for both Te NWs and Cu2−xTe NWs (Figure 2).

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242 were recorded in the temperature range from −190 °C to 530 °C (Figure 4). The laser power was set at ∼0.2 mW/μm² to minimize the laser-induced thermal effect. The low-frequency (50–300 cm⁻¹) Raman spectra of Cu₂₋ₓTe NWs present an obvious temperature dependence (Figure 4B,C). At 25 °C, weak Raman bands at (68, 116) cm⁻¹, 77 cm⁻¹, and 138 cm⁻¹ correspond to B₂g, B₃g, and Aₕ modes of Cu₂₋ₓTe NWs, respectively.15,34,35 By continuously lowering the temperature to −190 °C, the low-frequency Raman bands became gradually resolved along with the appearance of several new Raman bands at 84, 159, and 190 cm⁻¹, all of which are attributed to Eₕ asymmetry or symmetry modes due to the hexagonal-to-orthorhombic transition at low temperatures.41 The appearance of these new Raman bands originates from the symmetry change in the structural transition into the low-temperature orthorhombic phase. The gradual change in the Raman bands suggests that Cu₂₋ₓTe NWs undergo a second-order structural transition in the low-temperature region. Furthermore, we observed the initial Raman features of Cu₂₋ₓTe NWs when heated back to 25 °C from −190 °C (Figure S4). As can be seen in Figure 4B,C, a temperature increase beyond 25 °C gradually made these Raman bands weak and eventually disappear at 200 °C above. This may be ascribed to the thermally induced structural disordering with the increasing temperature. We observed a temperature region of featureless Raman spectra between 200 and 480 °C. Surprisingly, the continuing temperature increase beyond 480 °C produces a series of narrow Raman bands located at 60, 81, 269

Figure 4. In situ Raman measurements of Cu₂₋ₓTe NWs at temperatures between −190 °C and 530 °C. (A) (i) Schematic of the experimental setup for in situ Raman measurements and (ii) optical images of Cu₂₋ₓTe NW samples before and after the in situ Raman measurement. (B) False-color Raman map of Cu₂₋ₓTe NWs at temperatures between −190 and 530 °C. (C) Representative Raman spectra at selected temperatures from −190 to 530 °C. The temperature profile for in situ Raman measurements is shown in Figure S2. The measurements were started from 25 °C to −190 °C, to monitor the structural changes in the low-temperature region. All Raman spectra employed for construction of the false-color Raman map in B can be found in Figures S5 and S6. The dashed lines are guides to the eyes.

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Changes in these Raman spectra are greatly associated with the elemental Cu precipitation during the structural transition of Cu$_2$Te(s) $\rightarrow$ Cu$_{2-x}$Te(s) + Cu(s). The featureless Raman spectra indicate that the Cu$_2$Te NWs undergo an intermediate state of high degree of disorder before their dissociation at above 480 °C. The Cu precipitation behavior has been also suggested in the literature by theoretical calculations. The SEM image shows a large number of Cu nanoparticles attached around the Cu$_{2-x}$Te nanowires, demonstrating the precipitation of Cu nanoparticles at temperatures exceeding 480 °C, but the ICP-OES shows negligible change of the Cu:Te atomic ratio (~1.96) after the in situ Raman measurement (Figure S7). Similarly, a significant dark-to-yellow color change was observed after in situ Raman measurements (Figure 4A), indicating the irreversible structural transitions during the cooling–heating process. No significant change of the Raman shift position occurs during the cooling–heating process (Figure S8). The intensities of the characteristic Raman bands at 84, 116, 138, 190, and 712 cm$^{-1}$ were plotted against the temperature, as shown in Figure 5. A dramatic drop of Raman intensity is clearly observed for Raman bands at 84, 116, 138, and 190 cm$^{-1}$ with the temperature exceeding 20 °C. Negligible change occurs in the 200–480 °C temperature range, followed by a sudden intensity increase for all Raman bands at above 480 °C. The Raman band at 712 cm$^{-1}$ is invisible until above 480 °C. All Raman intensities are normalized by the maximum Raman intensity at 712 cm$^{-1}$ in the data set.

CONCLUSIONS

In conclusion, we have synthesized high-quality one-dimen-
sional nonstoichiometric Cu$_{2-x}$Te NWs and subsequently performed a systematic investigation on their thermally induced structural stability over a wide temperature range from −190 to 530 °C, using in situ Raman spectroscopy combined with in situ XRD measurements. The results demonstrate a dramatic temperature dependence of Raman spectra of Cu$_{2-x}$Te NWs and a remarkable correlation of the evolution of Raman signatures with their structural transitions. By lowering the temperature from 25 °C to −190 °C, broad low-frequency (50–300 cm$^{-1}$) Raman bands become gradually resolved with the appearance of new narrow Raman bands. Evolution of these Raman features with the temperature is attributed to the hexagonal weissite-to-orthorhombic transi-
tion. An intermediate state of high degree of disorder with featureless Raman spectra is observed between 200 and 480 °C, followed by the elemental Cu dissociation resulting from the dissociation of the high-temperature hexagonal Cu$_2$Te phase exceeding 480 °C. The results further show that changes in Raman bands including both the positions and intensity exactly follow the structural transitions of Cu$_{2-x}$Te NWs over the temperature range investigated. Our results demonstrate the advantages of in situ Raman spectroscopy for the in-depth understanding of thermal stability of Cu$_{2-x}$Te NWs over a...
Materials and Methods

Chemicals and Materials. Sodium tellurite (Na₂TeO₃, 99.9%), hydrazine hydrate solution (AR, 80%), acetone, and copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99.99%) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Ammonium hydroxide solution (AR, 25–28%) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Poly(vinylpyrrolidone) (PVP, (C₆H₉NO)ₓ, molecular weight ≈ 40 kg/mol), ethylene glycol ((C₂H₂OH)₂, 99.0%), and L-ascorbic acid (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Copper and tellurium standard solutions (1000 μg/mL for each) were purchased from Guobiao (Beijing) Testing and Certification Co., Ltd. (Beijing, China). Anhydrous ethanol (AR, ≥ 99.9%) was ordered from Shanghai Titan Scientific Co., Ltd. (Shanghai, China). Ultrapure water (18.2 MΩ·cm) was produced with a Millipore Direct-Q3 UV system (Millipore Corporation, Molsheim, France) and used throughout the experiments. All chemicals and solvents were of analytical grade and used as received.

Synthesis of Te Nanowires. Te NWs were synthesized by a hydrothermal method according to a previously published protocol with slight modifications.28,36 Typically, 1.0 g of PVP was first dissolved in 33 mL of ultrapure water, followed by the dissolution of 92.2 mg of Na₂TeO₃ to obtain a clear solution. Then, 3.33 mL of ammonium hydroxide solution and 1.67 mL of hydrazine hydrate were sequentially added to the above solution under magnetic stirring. The solution was then transferred into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was kept at 180 °C for 3 h to allow the full conversion of the Te precursor to Te NWs. The resulting Te NWs were precipitated by acetone and washed at least three times sequentially with ultrapure water and ethanol. Finally, the resulting Te NWs were dried at 60 °C in a vacuum oven and redispersed in 30 mL of ethylene glycol for the following use.

Synthesis of Cu₂₋ₓTe Nanowires. Cu₂₋ₓTe NWs were prepared by the direct conversion of Te NWs in the presence of the copper precursor with the reducing agent ascorbic acid.29 Specifically, the copper precursor solution was first prepared by dissolving 48.3 mg (0.20 mmol) of Cu(NO₃)₂·3H₂O into 1.0 mL of ethylene glycol. The copper precursor solution was dropwise added to 10 mL of the ethylene glycol solution of Te NWs obtained above, followed by the rapid addition of 0.6 mL of ascorbic acid aqueous solution (1.89 M). After the reaction proceeded at room temperature for 1 h, the products were washed at least twice with ultrapure water and then dispersed in ultrapure water for further use.

Characterization. Scanning electron microscopy (SEM) images were taken using an FEI Helios Nanolab G3 UC dual-beam scanning electron microscope system (FEI, Czech Republic). Transmission electron microscopy (TEM) images were acquired on an FEI Tecnai G2 F20 transmission electron microscope (FEI, USA) operating at 200 kV. The TEM samples were prepared by dropping the colloidal suspension on a thin carbon-coated 300 mesh copper grid (Beijing Zhongjingkeyi Technology Co. Ltd., China), followed by being dried in the air. Diameter distribution of Te and Cu₂₋ₓTe NWs was determined from the TEM data using the ImageJ analysis software. At least 100 nanowires were counted for each type of samples, and Gaussian fitting was carried out to obtain the mean diameter of NWs. Absorption spectra were recorded in a transmission mode using the colloidal suspensions in the wavelength range of 300–800 nm on an Agilent Cary 5000 UV–vis–NIR spectrophotometer (Agilent Technology, USA). The elemental composition of Cu₂₋ₓTe NWs was determined through inductively coupled plasma-optical emission spectroscopy (ICP-OES) on an Agilent 7100 inductively coupled plasma–optical emission spectrometer (Agilent Technologies, USA). For the sample preparation of ICP-OES measurements, Cu₂₋ₓTe NWs were washed and dispersed into ultrapure water and then digested in aqua regia to obtain a clear solution. The emission lines at 214.282 and 324.754 nm were employed for the concentration determination of Te and Cu, respectively.

In Situ Raman and XRD Measurements. Raman spectra were collected on a Renishaw inVia Raman microscope system equipped with a Leica DM2700 M Ren RL/TL microscope. The CCD detector has holographic grating with 1800 lines/mm, and the calibration of the spectrum was carried out using a Raman peak of silicon at 520.5 cm⁻¹ prior to the Raman measurement. Raman spectra were acquired with an ×50L objective (NA 0.5), 0.2 mW of 532 nm laser excitation on the samples, and acquisition time of 1 s. For in situ Raman measurements, the temperature was controlled with a Linkam THMS 600 heating and freezing stage system consisting of a THMS 600 stage, a T95 system controller, and an LNPF5 liquid nitrogen cooling pump. The Cu₂₋ₓTe powder sample was placed in a quartz crucible and heated to the temperature between −190 and 530 °C with a ramp rate of 2.0 °C/min, followed by the Raman measurements.

In situ XRD measurements were performed on a SmartLab3 kW X-ray diffractometer (Rigaku, Japan) using Cu Kα (λ = 1.5406 Å) radiation operating at 40 kV and 30 mA. An Anton Paar TTK 600 chamber was used to control the temperature. XRD patterns were collected in the 2θ range of 20–70° with a step size of 0.02° between −190 and 530 °C.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b08427.

The calibration curves for the Cu and Te concentration–emission intensity for quantification by ICP-OES; temperature profile for in situ XRD measurements at temperatures between −190 and 530 °C; the temperature profile for in situ Raman measurements of Cu₂₋ₓTe nanowires adopted in this work; Raman spectra of Cu₂₋ₓTe nanowires at 25 °C; evolution of Raman spectra of Cu₂₋ₓTe nanowires in the temperature range from −190 to 200 °C; evolution of Raman spectra of Cu₂₋ₓTe nanowires in the temperature range from 200 to 530 °C; SEM image of Cu₂₋ₓTe nanowires after the in situ Raman measurement; Raman shift position of Cu₂₋ₓTe nanowires as a function of temperature (PDF)
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