Lanthanum Telluride Nanowires: Formation, Doping, and Raman Studies

A. K. Samal and T. Pradeep*

DST Unit on Nanoscience (DST UNS), Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology, Madras, Chennai, 600 036 India

Received: December 9, 2009; Revised Manuscript Received: February 24, 2010

A new approach for the synthesis of freely dispersible one-dimensional (1D) lanthanum telluride nanowires (La₂Te₃ NWs) in the solution phase is reported. The process involves a reaction between tellurium nanowires (Te NWs) and lanthanum nitrate (La(NO₃)₃) at room-temperature. Te NWs act as templates for the formation of La₂Te₃ NWs. The aspect ratio of the as prepared La₂Te₃ NWs is the same as the parent Te NWs. Various microscopic and spectroscopic tools such as HRTEM, SEM, EDAX, XRD, XPS, Raman, UV–visible, and fluorescence were used for the characterization of the NWs. A new surface enhanced Raman active substrate was synthesized by doping silver in La₂Te₃ NWs. Surface enhanced Raman spectra were studied using crystal violet (CV) as the analyte. Raman features have been observed up to a concentration of 10^{-8} M of CV. Different concentrations of Ag in Ag-doped La₂Te₃ NWs were investigated. The monodispersity, homogeneity, and Raman enhancement properties of the NWs, synthesized through a simple solution phase protocol, are expected to motivate further studies on this material.

Introduction

Semiconducting tellurides are receiving considerable attention because of their potential applications in electronics, optoelectronics, and thermoelectrics as well as in biological and magnetic sensors.¹⁻⁵ Some of these properties are enhanced in low dimensional tellurides due to quantum confinement. Therefore, it is essential to develop facile methods to synthesize diverse telluride nanostructures. Among the structures, 1D tellurides are important from various perspectives. Different methods such as hydrothermal, solvothermal, chemical vapor transfer, electrodeposition, sonoelectrochemistry, and template based methods are employed to synthesize 1D tellurides.^{6–11} Apart from these, self-sacrificing template technique is the straightforward strategy for the synthesis of 1D tellurides using 1D nanostructures as the template. Considering the reduction potential of TeO_3^{2-}/Te system (0.589 V) with other metals, tellurium nanostructures can be used as templates to form various tellurides.¹² Telluride nanotubes such as CoTe₂ and CoTe were synthesized using Te nanotubes and nanorods, respectively as templates.^{13,14} Te NWs are potentially used as self-sacrificial templates to form different composite NWs because the morphology of the formed telluride may be similar to the original one used. For example, Ag₂Te NWs have been synthesized at room temperature using Te NWs as the template.¹⁵ Highly uniform CdTe and PbTe NWs with a very high aspect ratio of ~ 1000 were synthesized using ultrathin Te NWs as templates.¹⁶ Rare-earth metal tellurides are of interest in solid state chemistry and materials science because of their physical properties and rich structural chemistry. These tellurides have very significant structural, electronic, optical, and magnetic properties.^{17–22} Among these rare earth tellurides, lanthanum tellurides are known to show thermoelectric properties and are important for applications due to their high thermal stability.²³ Various properties associated with lanthanum tellurides such as structural, electronic, optical, and transport properties are discussed elsewhere.24-28

Bulk $La_{3,x}Te_4$ was synthesized by chemical alloying, in which lanthanum and tellurium were mixed in high energy ball mills.²³ La_2Te_3 thin film was synthesized by spray pyrolysis, where lanthanum salt and Te powders were used.²⁹ LaTe₂ and LaTe₃ were synthesized by the self-flux technique.^{26,30} Different molar ratios of lanthanum and tellurium were heated at high temperature in a sealed quartz tube over a period of 3–4 days. In the present report, we present a simple chemical synthesis route for making La_2Te_3 NWs in the solution phase at room temperature. Te NWs were synthesized and used as templates for the formation of La_2Te_3 NWs. We believe that this is the first report of the synthesis of this material in the nanoscale, enabling further studies and applications.

Doping of Ag in tellurides is known to alter their crystal structures which lead to changes in the characteristic properties.^{31–34} Doping of Ag in the ternary compound, PbBi₄Te₇, enhances the Seebeck coefficient by reducing its lattice thermal conductivity and increasing the electrical conductivity.³¹ Doping of Ag in Sb₂Te₃ and Bi₂Te₃ reportedly alters their crystal structures.³² Lostak et al. have studied the effect of Ag-doping in Sb₂Te₃ and observed defects in the crystals which strongly influence the transport properties.³³ Increase in the concentration of Ag in the Sb₂Te₃ system leads to decrease in the Hall effect and Seebeck coefficient as well. CdTe thin films doped with Ag change the shape and size of the grain structure vis-à-vis the parent material.³⁴ Hall measurement of Ag-doped CdTe suggests an increase in the mobility and carrier concentration of the thin films. We report here the utility of Ag-doped La₂Te₃ NWs for enhanced Raman activity. Doping of Ag leads to a significant increase in the Raman activity of the substrate. The Raman spectrum is observable up to a concentration 10^{-8} M of CV, used as the analyte.

Experimental Section

Sodium dodecyl sulfate (SDS, $C_{12}H_{25}O_4SNa$, 99%) was obtained from Acros. Tellurium dioxide (TeO₂, 99.9%) powder was purchased from Alfa Aesar. Silver nitrate (AgNO₃), lanthanum nitrate (La(NO₃)₃•6H₂O), and hydrazine monohy-

^{*} To whom correspondence should be addressed. E-mail: pradeep@ iitm.ac.in. Fax: 91-44-2257-0545/0509.

drate (N_2H_4 • H_2O , 99–100%) were purchased from SD Fine Chemicals, India. Deionized water was used throughout the experiment.

Synthesis of La_2Te_3 NWs was carried out in two steps: (1) synthesis of Te NWs and (2) the reaction between Te NWs and $La(NO_3)_3$. Te NWs were prepared by the wet chemical method, reported by Chang et al.³⁵ In a reaction, 16 mg of TeO₂ powder was slowly added to a beaker containing 10 mL of hydrazine hydrate. The reaction was allowed to continue at room temperature under constant stirring. The powder was completely dissolved and the color of the solution changed from colorless to blue after 1 h which indicates the formation of Te NWs. After 1 h, the solution was diluted 10-fold with 10 mM SDS, in order to control the length of the NWs. The as prepared solution was purified by centrifugation at 18 000 rpm for 10 min to remove excess hydrazine and SDS. The residue was redispersed in deionized water and centrifuged twice for the complete removal of unreacted species.

For the synthesis La_2Te_3 NWs, 10 mL of $La(NO_3)_3$ (10 mM) was added to 90 mL of the purified Te NWs and stirred for 24 h. The color changed from blue to black. The product was centrifuged at 18 000 rpm for 10 min, and the process was repeated twice for the complete removal of unreacted species. The residue was redispersed in deionized water for further characterization. La_2Te_3 NWs powder was prepared by freezedrying the concentrated solution for further studies. Ag-doped La_2Te_3 NWs were synthesized by adding AgNO₃ (1 mL, 10 mM) to 9 mL of purified La_2Te_3 NWs. The mixture was allowed to stir for 24 h. The product was centrifuged to remove unreacted species and characterized by various techniques.

Instrumentation. UV-visible absorption spectra were recorded using Perkin-Elmer Lambda 25 spectrophotometer in the range of 200-1100 nm. High-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray analysis (EDAX) were carried out with an Oxford EDAX housed in a JEOL 3010, 300 kV instrument equipped with a UHR pole piece. The samples were prepared by dropping the dispersion on carbon coated copper grids and drying in ambience. Scanning electron microscopy (SEM) and EDAX were carried out using a FEI QUANTA-200 SEM instrument. Samples were prepared on conducting ITO glass plates. X-ray diffraction (XRD) data were collected with a Shimadzu XD-D1 diffractometer using Cu K α ($\lambda = 1.54$ Å) radiation. The samples were scanned in the 2θ range of $10-90^{\circ}$. All of the peaks were assigned and compared with the database published by the Joint Committee on Power Diffraction Standards (JCPDS). Fluorescent measurements were carried out using a HORIBA JOBIN VYON NanoLog fluorescence spectrofluorimeter. X-ray photoelectron spectroscopy (XPS) measurements were done using an Omicron ESCA Probe spectrometer with polychromatic Mg K α X-rays (hv = 1253.6 eV). Raman spectra were studied using WiTec GmbH confocal micro Raman equipped with a CCD detector. The light source was a Nd:YAG laser of 532 nm wavelength.

Results and Discussion

Te NWs are known to have two characteristic absorption peaks: peak I and peak II. Peak I is due to the transition from p-bonding valence band (VB2) to the p-antibonding conduction band (CB1) and it appears in the range of 250-350 nm. Peak II is due to the transition from p-lone pair valence band (VB3) to the p-antibonding conduction band (CB1) and it appears around 600-850 nm.³⁵⁻³⁷ In this particular synthesis, peak I appeared at 284 nm and peak II appeared at 716 nm (Figure

1A). XRD pattern of Te NWs is shown in Figure 1B. All of the peaks of the Te NWs were indexed to the hexagonal phase of Te. The unit cell constants are a = 0.4451 nm and c = 0.5904nm, which are consistent with the literature data (JCPDS: 36-1452). Figure 1C shows a high magnification TEM image of a single NW suggesting the straight morphology of the NWs. Large area TEM image of Te NWs is shown in Figure 1D. Length of the Te NWs was found to be $\sim 670-700$ nm with a width of $\sim 20-25$ nm. Lattice resolved HRTEM image of a single Te NW (Figure 1E) shows the interplanar spacings of 0.59, 0.39, and 0.22 nm which correspond to (001), (010), and (110), respectively.³⁵ All the NWs were straight and have uniform morphology. There was no dislocation and planar defects on the NWs, which suggest that the NWs are single crystalline.

After the reaction with La(NO₃)₃, the product was purified and redispersed with deionized water and characterized by various techniques. The absorption spectrum of La₂Te₃ NWs shows a substantial change in both the peaks compared to the parent NWs. Peak I shows a red shift from 284 to 294 nm and peak II shows a shift from 716 to 734 nm (Figure 2A). XRD pattern of La₂Te₃ is shown in Figure 2B. All peaks in the XRD pattern were indexed to the cubic phase of La₂Te₃ whose unit cell parameter is a = 0.949 nm, which is consistent with the literature data (JCPDS: 19-0662). The noticeable changes observed from the reactants to the products are that straight NWs got slightly bent and a structural change occurred from a hexagonal phase (Te NWs) to a cubic phase. Figure 2C shows the spectral change observed by the addition of different concentrations of La(NO₃)₃. Calculated amounts of La³⁺ were added to the purified Te NWs to obtain the required concentration, as indicated in the figure. The spectral changes occurred at different concentrations were studied after 24 h. Purified Te NWs show two peaks at 284 and 716 nm. After the addition of 0.1 mM of La³⁺, both the peaks were red-shifted. Peak I shifted to 286 nm and peak II shifted to 719 nm. With further increase in the concentration of La³⁺, peaks I and II further red-shifted. When the concentration was 1 mM, peak I reached a maximum of 294 nm and peak II reached a value of 734 nm. Figure 2D shows the time-dependent absorption spectral changes corresponding to 1 mM of La³⁺. At 1 h, peak I shifted to 290 nm whereas peak II was observed at 718 nm. Peak shifts continued upon increasing the reaction time. After 24 h, no further change was observed. As mentioned in the experimental section, the sample corresponding to 10 mM of La³⁺ was used for all the subsequent measurements.

TEM images of La₂Te₃ NWs at different magnifications are shown in Figure 3. Figure 3A shows its large area TEM image. It shows that the NWs are slightly bent. Figure 3B shows the lattice resolved HRTEM image of the body of a single La2Te3 NW. The interplanar spacings of 0.33 and 0.19 nm correspond to the (220) and (422) lattice plane of La₂Te₃ NWs, respectively. The aspect ratio of La2Te3 NWs was found to be the same as that of Te NWs. Large area SEM image of La₂Te₃ NWs is shown in Figure 3C. Similar morphology was observed in TEM. Figure 3D shows the SEM-EDAX spectrum of La₂Te₃ NWs, indicating the presence of La and Te quantitatively. The presence of Si and Sn peaks are due to the indium tin oxide conducting glass plate used as the substrate for the EDAX measurement. Elemental analysis and TEM-EDAX spectrum of La₂Te₃ NWs are shown in Figure 4 which confirms the chemical composition. Elemental maps of La and Te are shown in Figure 4, panels B and C, respectively. The TEM image corresponding to the elemental maps is shown in Figure 4A. Atomic ratio of La to



Figure 1. UV-visible spectrum of purified Te NWs (A), XRD pattern of hexagonal Te (B), high magnification TEM image of single Te NW suggesting the straight morphology (C), large area TEM image of Te NWs (D) and lattice resolved HRTEM image of the body of a single NW (E). Inset shows the FFT image of corresponding HRTEM.



Figure 2. UV-visible spectrum (A), XRD pattern (B), concentration (C), and time-dependent (D) absorption spectra, respectively, of La₂Te₃ NWs.

Te obtained from quantitative analysis of La L α and Te L α of the EDAX spectrum shown in Figure 4D is 1.99:3.00, indicating that the stoichiometric composition is 2:3.

Te NWs are semiconducting, known to show luminescence depending upon the aspect ratio of the NWs.³⁶ Luminescence

spectra of Te NWs and La_2Te_3 NWs were measured. The excitation and emission were at 352 and 393 nm, respectively, for Te NWs. Both the excitation and emission spectra showed a red-shift compared to the parent Te NWs. Excitation spectrum showed a shift of 9 nm and was observed at 361 nm. Emission



Figure 3. (A) Large area TEM image of La_2Te_3 NWs, (B) lattice resolved HRTEM of the body of a single La_2Te_3 NW, (C) large area SEM image of La_2Te_3 NWs, and (D) EDAX spectrum La_2Te_3 NWs. Si and Sn peaks in D are due to the indium tin oxide conducting glass plate used as the substrate for SEM measurements. Inset shows the FFT image of corresponding HRTEM.



Figure 4. TEM image used for elemental mapping (A) and elemental maps using Te L α (B) and La L α (C) of La₂Te₃ NWs. EDAX spectrum of La₂Te₃ NWs is shown in (D). Cu and Si peaks in D are due to the grid and S peak is due to the surfactant, SDS.

spectrum was found to shift by 6 nm and was observed at 399 nm. Excitation and emission spectra of Te and La_2Te_3 NWs are shown in Figure 5A. Red-shift of La_2Te_3 NWs may be attributed to the reaction between $La(NO_3)_3$ and Te NWs.

The chemical composition of the sample was confirmed from the XPS spectrum. XPS of La_2Te_3 NWs shows the presence of small amount of oxides. The survey spectrum is shown in Figure 5B. Expanded scans of the spectrum in the La 3d and Te 3d regions are shown in Figure 5C and 5D, respectively. La 3d splits into two main peaks, $3d_{5/2}$ and $3d_{3/2}$ due to spin-orbit interaction. Each of these peaks is a doublet of comparable intensity. The weaker satellite peaks are believed to be due to the charge transfer process.³⁸ Such splitting of the main peaks has been observed in trivalent lanthanum compounds such as



Figure 5. (A) Luminescence spectra of Te NWs and La_2Te_3 NWs, (B) XPS survey spectrum of La_2Te_3 NWs, (C) expanded scans in the La 3d, and (D) Te 3d regions showing the presence of oxides. Spectra in C and D are background corrected.



Figure 6. Raman spectra of Te NWs and La₂Te₃ NWs.

halides,³⁹ oxides,^{39,40} and sulphides.⁴¹ These satellite peaks are observed due to the transfer of an electron from O 2p to the empty 4f shell of La leading to the $3d^94f^1$ final state.⁴² The binding energies 834.7 and 851.5 eV for the main peaks and 838.0 and 854.9 eV for the satellite peaks agree well with the earlier reports of La in the +3 oxidation state.^{43–45} Te 3d region has two sets of peaks showing the existence of Te^{2–} in La₂Te₃ and Te⁴⁺ due to a surface oxide layer. The peaks observed at 571.6 and 582.0 eV correspond to 3d binding energy of Te^{2–} (Figure 5D). The less intense peaks at 575.6 and 586.1 eV are attributed to Te (IV) oxide. The XPS data are similar to those systems containing Te^{2-} and Te^{4+} , reported previously.^{46,47} The quantification of peaks indicates a stoichiometry ratio of La to Te of 2:3.

The Raman spectra of Te NWs and La₂Te₃ NWs were investigated (Figure 6). Te NWs show three intense Raman peaks at 149, 267, and 479 cm⁻¹. The peak at 149 cm⁻¹ can be assigned to the lattice vibration of Te NWs. The peak at 267 cm⁻¹ can be assigned either to the Te–O vibration⁴⁸ arising from the thin oxide layer formed upon exposure of laser or due to Te-sulfate vibration from the stabilizing SDS. The peak at 479 cm⁻¹ can be assigned to the Te–O vibration of the oxide layer. The two peaks observed in La₂Te₃ NW at 406 and 716 cm⁻¹ may be due to the thin layer of oxides formed on the surface of the NWs. This was confirmed from the following experiment. Upon immediate exposure of laser on La₂Te₃ NWs, two broad peaks at 375 and 699 cm⁻¹ appeared. With increasing exposure time, the peak intensity increases and the peaks shifted to higher wavenumbers. This may be attributed to the formation of oxides on the surface of the NWs. Upon exposure of the laser for 5 min, two broad peaks appeared at 396 and 699 cm⁻¹. These two peaks may be assigned to the stretching modes, Te-O of TeO₂. On exposure for 10 min, the peaks broadened with maxima at 406 and 716 cm⁻¹. Raman peaks of lanthanum oxide (La₂O₃) are observed at 105, 192, and 406 cm^{-1.⁴⁹ Among} these, a strong peak of La_2O_3 was observed in the range of 404-409 cm^{-1, 50-54} The peak at 406 cm⁻¹ upon 10 min exposure can therefore be assigned to the La-O vibration. Raman spectrum of TeO₂ is known to show peaks in the range of $200-800 \text{ cm}^{-1}$.⁴⁸ The broad peak obtained at 716 cm⁻¹ can be assigned to the symmetric stretching of Te-O of TeO₂.55 The presence of tellurium oxide in the Raman spectrum is consistent with the XPS data shown in Figure 5C.



Figure 7. Large area TEM image of Ag-doped La₂Te₃ NWs (A) and lattice resolved HRTEM image of the body of a single NW (B). Inset shows the FFT image of corresponding HRTEM.



Figure 8. Elemental mapping of Ag-doped La₂Te₃ NWs using (A) Ag L α , (B) La L α , and (C) Te L α . Scale bar is 50 nm. (D) EDAX spectrum Ag-doped La₂Te₃ NWs.

Two mechanisms have been proposed to understand the formation of 1D metal tellurides from Te NWs.^{16,56} In the first self-sacrificial process, elemental Te simultaneously oxidizes and reduces to Te^{4+} and Te^{2-} and the latter species reacts with metal ions to form metal tellurides. In the second process, metal ions are reduced to atoms first, which then react with Te NWs in situ to generate metal telluride. The first process, resembles disproportionation and is expected to be energy intensive, especially at room temperature. The standard reduction potentials of TeO_3^{2-}/Te , La^{3+}/La , and N_2/N_2H_4 are 0.589, -2.379, and -1.15 V, respectively. Therefore, the reduction of lanthanum in solution is very difficult. Therefore, it appears that adsorption of metal ions on the Te NW template, followed by surface reduction is the likely event. Residual hydrazine at the surface might be facilitating this process. The presence of hydrazine is confirmed by the N1s signature in the XPS spectrum of La₂Te₃ (Figure S3A). Note that no external hydrazine was added into Te NWs for the formation of La₂Te₃. Therefore, the hydrazine present has to come from Te NWs.

For doping of Ag to La₂Te₃ NWs, AgNO₃ (1 mL, 10 mM) was added to 9 mL of purified La₂Te₃ NW suspension and

stirred for 24 h. The product was purified by centrifugation and redispersed in deionized water. The absorption spectrum of Agdoped La2Te3 NWs shows the disappearance of two peaks. A new peak appeared around at 500 nm (Figure S1). The XRD pattern of the centrifuged powder is shown in Figure S2. All of the XRD peaks were indexed to the cubic phase of La₂Te₃ (JCPDS: 19–0662) and the monoclinic phase of Ag₂Te (JCPDS: 34-0142), although there are slight differences in intensities. TEM images of Ag-doped La2Te3 NWs at different magnifications are shown in Figure 7. Figure 7A shows a large area TEM image which shows the same aspect ratio and similar morphology as of La₂Te₃ NWs. Some surface roughness is seen in the NWs. Figure 7B shows a lattice resolved HRTEM image of a single Ag-doped La2Te3 NW. The interplanar spacing 0.39 and 0.67 nm correspond to (211) and (101) planes La₂Te₃ and Ag₂Te, respectively, in accordance with the XRD pattern (Figure S2). Figure 8 shows the presence of Ag, La, and Te in individual NWs. EDAX spectrum is shown in Figure 8D. In view of the presence of Ag, La, and Te in the same NW, we suggest that Ag₂Te and La₂Te₃ domains are present in the same NW. This implies that either La has to get depleted in the NW or Te has



Figure 9. SERS spectra of Ag-doped La₂Te₃ NWs (A) different concentrations of CV and (B) different concentrations of Ag at 10⁻⁶ M of CV.

to get incorporated into the NW along with Ag so that stoichiometry is maintained. As the thickness of the Ag-doped La_2Te_3 is not significantly different from the parent La_2Te_3 NW, we suggest that the surface oxide of Te present on La_2Te_3 NW got reduced. It is likely that this surface reduction is facilitated by the residual hydrazine present in the parent La_2Te_3 NWs. Evidence for this is seen in XPS. In La_2Te_3 NWs, N 1s is seen at 400.0 eV. However, this is absent in Ag-doped La_2Te_3 NWs (Figure S3). This can be attributed to the loss of adsorbed hydrazine consumed during the reduction of the surface oxide layer. In agreement with this, the intensity of Te 3d due to Te⁴⁺ in the Ag-doped sample is less than that of parent La_2Te_3 NWs, measured under identical conditions. A comparison of the two is presented in Figure S4.

Among the various detection tools, SERS is one of most important techniques to provide vibrational information when molecules are adsorbed on metallic nanostructures.^{57,58} Semiconducting NWs can be considered as ideal materials for sensing and detection, due to the large surface area of the NWs available for interaction with analyte species and also due to the semiconducting properties, which may be used for signal extraction. SERS is a highly sensitive analytical technique in the area of nanoscale materials where molecular information from chemical and biological systems is detected at ultra low concentrations.⁵⁹⁻⁶¹ Detection of ultra low concentrations is possible with a Raman enhancement factor of 10¹⁴ to 10¹⁵.62,63 It is known that the largest enhancement occurs when the molecule sits on roughened surfaces of coinage metals such as Au, Ag, and Cu. Among these metals, silver in different forms such as silver nanoparticles, aggregates, periodic arrays, and thin films is known to show high SERS activity.⁶⁴ Ag-doped MnO₂ formed hierarchical flower-like nanostructures which exhibit SERS using rhodamine 6G (R6G) and 2-aminothiophenol (ATP) as the probe molecules.⁶⁵ Ag nanoparticles deposited on silicon NWs showed SERS with a detection limit 10^{-14} M using R6G as the probe molecule.⁶⁶ Silver cluster doped silica colloids also showed SERS.⁶⁷ Ag-doped 7-azaindole, a heterocyclic DNA model compound showed SERS and the observed enhancement factor was on the order of 10⁴.⁶⁸ Recently, an SERS active substrate was synthesized using gold on Te NWs forming hybrid materials.⁶⁹ We investigated the SERS activity of Ag-doped La₂Te₃ NWs by using CV as the analyte. It was observed that Raman signals enhanced by increasing the concentration of Ag on La2Te3 NWs. Different concentrations of Ag and CV were studied on doped La₂Te₃ NWs.

For SERS measurements, an Ag-doped (using 1 mM AgNO₃) La₂Te₃ NW substrate was immersed in CV solution of varying concentrations for 3 h. The substrate was washed gently with distilled water and dried. A laser of 532 nm wavelength was used throughout the experiment. Raman spectra of CV at different concentrations adsorbed on Ag-doped La₂Te₃ NWs as well as undoped La2Te3 NWs were measured. Different concentrations of CV such as 10^{-5} , 10^{-6} , 10^{-7} , and 10^{-8} M were used. Figure 9A shows the distinct Raman features of adsorbed CV on Ag-doped La2Te3 even at a concentration of 10⁻⁸ M. At the same time, no Raman features were observed from the surface of blank La₂Te₃ NWs (the trace of undoped La₂Te₃ in Figure 9A) even at a higher concentration of CV (10^{-6} M). It is observed that the peak intensity of CV depends linearly on the concentration of CV used. The enhancement of Raman spectra of different concentrations of Ag on La₂Te₃ NWs of adsorbed CV were studied (Figure 9B). The concentration of CV was 10⁻⁶ M. Calculated amounts of AgNO₃ were added to La₂Te₃ NWs to obtain the required concentration, as indicated in the figure. With the increase in the concentration of Ag on La₂Te₃, the Raman features of CV were enhanced in SERS. Elemental mapping of Ag-doped La2Te3 NWs revealed that Ag was present throughout the NWs (Figure 8). Uniform distribution of Ag throughout the NWs may be providing SERS active sites. SERS enhancement of silver NWs was largely on the tips upon irradiation of the laser.⁷⁰ It is due to the 'hot spots' of the NWs created when they come closer and arrange in an end-toend fashion forming junctions. SERS enhancement of hot spots decreases when the interparticle distance increases. The possibility of sidewise or crosswise arrangement of these NWs after drying on the cover glass cannot be avoided in a typical sample. The enhancement of the NWs when arranged in sidewise can be explained on the basis of pairwise electromagnetic interaction.⁷¹ Similarly, enhancement upon crosswise arrangement can also be understood.⁷²

Conclusion

La₂Te₃ and Ag-doped La₂Te₃ NWs were synthesized by wet chemical synthesis in solution phase using Te NWs as the template at room temperature. La₂Te₃ NWs were characterized by microscopic and spectroscopic tools. XRD, HRTEM, SEM, EDAX, Raman, and XPS reveal the structure and composition of the materials. Ag was doped in La₂Te₃ NWs and the product acts as SERS active substrates, using CV as the analyte. SERS activity of the NWs was studied at different concentrations of CV and Ag on La₂Te₃ NWs. The cost-effective, one-pot synthesis and enhanced Raman activity of the material are expected to motivate the exploration of their properties and applications.

Acknowledgment. We thank the Nano Mission of the DST, Government of India for continuously supporting our research program.

Supporting Information Available: UV-visible and XRD of Ag-doped La2Te3 NWs as well as XPS of La2Te3 and Agdoped La₂Te₃ NWs in the N 1s and Te 3d regions. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

- (1) Trudeau, P. E.; Sheldon, M.; Altoe, V.; Alivisatos, A. P. Nano Lett. 2008, 8, 1936.
- (2) Wu, Q.; Litz, M.; Zhang, X. C. Appl. Phys. Lett. 1996, 68, 2924. (3) Venkatasubramanian, R.; Siivola, E.; Colpitts, T.; Quinn, B. O. Nature 2001, 413, 597.
- (4) Wang, S. P.; Mamedova, N.; Kotov, N. A.; Chen, W.; Studer, J. Nano Lett. 2002, 2, 817.
- (5) Hussmann, A.; Betts, J. B.; Boebinger, G. S.; Migliori, A.; Rosenbaum, T. F.; Saboungi, T. F. Nature 2002, 417, 421.
- (6) Qin, A. M.; Fang, Y. P.; Tao, P. F.; Zhang, J. Y.; Su, C. Y. Inorg. Chem. 2007, 46, 7403.
- (7) Li, Y. D.; Ding, Y.; Wang, Z. Y. Adv. Mater. 1999, 11, 847.
- (8) Fardy, M.; Hochbaum, A. I.; Goldberger, J.; Zhang, M. M.; Yang, P. Adv. Mater. 2007, 19, 3047.
 - (9) Chen, R.; Xu, D.; Guo, G.; Gui, L. J. Mater. Chem. 2002, 12, 2435.
- (10) Qiu, X.; Lou, Y.; Samia, A.; Devadoss, A.; Burgess, J.; Dayal, S.; Burda, C. Angew. Chem., Int. Ed. 2005, 44, 5855.
- (11) Sapp, S. A.; Lakshmi, B. B.; Martin, C. R. Adv. Mater. 1999, 11, 402.
- (12) Wang, Y.; Tang, Z.; Podsidlo, P.; Elkasabi, Y.; Lahann, J.; Kotov, N. A. Adv. Mater. 2006, 18, 518.
- (13) Li, J.; Tang, X.; Song, L.; Zhu, Y.; Qian, Y. J. Cryst. Growth 2009, 311. 4467.
- (14) Fan, H.; Zhang, Y. G.; Zhang, M. F.; Wang, X. Y.; Qian, Y. T. Cryst. Growth Des. 2008, 8, 2838.
- (15) Samal, A. K.; Pradeep, T. J. Phys. Chem. C 2009, 113, 13539.
- (16) Liang, H. W.; Liu, S.; Wu, Q. S.; Yu, S. H. Inorg. Chem. 2009, 48, 4927.
 - (17) Mitchell, Kwasi.; Ibers, J. A. Chem. Rev. 2002, 102, 1929.
- (18) Narducci, A. A.; Yang, Y.; Digman, M. A.; Sipes, A. B.; Ibers, J. A. J. Alloys Compd. 2000, 303, 432.
- (19) Yao, J.; Deng, B.; Sherry, L. J.; McFarland, A. D.; Ellis, D. E.; Van Duyne, R. P.; Ibers, J. A. Inorg. Chem. 2004, 43, 7735.
 (20) Liu, Y.; Chen, L.; Wu, L. M. Inorg. Chem. 2008, 47, 855.

 - (21) Ijjaali, I.; Ibers, J. A. J. Solid State Chem. 2006, 179, 3456.
- (22) Liu, M. L.; Wu, L. B.; Huang, F. Q.; Chen, L. D.; Ibers, J. A. J. Solid State Chem. 2007, 180, 62.
- (23) May, A. F.; Fleurial, J. P.; Snyder, G. J. Phy. Rev. B 2008, 78, 125205.
 - (24) Stowe, K. J. Solid State Chem. 2000, 149, 155.
 - (25) Kwon, Y. S.; Min, B. H. Physica B 2000, 281, 120.
- (26) Shin, K. Y.; Brouet, V.; Ru, N.; Shen, Z. X.; Fisher, I. R. Phys. Rev. B 2005, 72, 085132.
- (27) Jung, M. H.; Kwon, Y. S.; Kinoshita, T.; Kimura, S. Physica B 1997, 230, 151.
 - (28) Ru, N.; Fisher, I. R. Phys. Rev. B 2006, 73, 033101.
- (29) Bagde, G. D.; Sartale, S. D.; Lokhande, C. D. Mater. Chem. Phys. 2005, 89, 402.
 - (30) Ru, N.; Fisher, I. R. Phy. Rev. B 2006, 73, 033101.
- (31) Shelimova, L. E.; Karpinskii, O. G.; Svechnikova, T. E.; Nikhezina, I. Y.; Avilov, E. S.; Kretova, M. A.; Zemskov, V. S. Inorg. Mater. 2008, 44, 371.

- (32) Navratil, J.; Klichova, I.; Karamazov, S.; Sramkova, J.; Horak, J. J. Solid State Chem. 1998, 140, 29.
- (33) Lostak, P.; Drasar, C.; Horak, J.; Zhou, Z.; Dyck, J. S.; Uher, C. J. Phys. Chem. Solids 2006, 67, 1457.
- (34) Shah, N. A.; Ali, A.; Aqili, A. K. S.; Maqsood, A. J. Cryst. Growth 2006, 290, 452.
- (35) Lin, Z. H.; Yang, Z.; Chang, H. T. Cryst. Growth Des. 2008, 8, 351
- (36) Sreeprasad, T. S.; Samal, A. K.; Pradeep, T. J. Phys. Chem. C 2009, 113, 1727.
- (37) Gautama, U. K.; Rao, C. N. R. J. Mater. Chem. 2004, 14, 2530. (38) Jorgensen, C. K.; Berthou, H. Chem. Phys. Lett. 1972, 13, 186.
- (39) Signorelli, A. J.; Heyes, R. G. Phys. Rev. B 1973, 8, 81.
- (40) Schneider, W. D.; Delley, B.; Wuilound, E.; Imer, J. M.; Bear, Y. Phys. Rev. B 1985, 32, 6819.
- (41) Kaciuilis, S.; Latisenka, A.; Plesanovas, A. Surf. Sci. 1991, 251-252, 330.
- (42) Fuggle, J. C.; Campagna, M.; Zolnierek, Z.; Lasser, R.; Platau, A. Phys. Rev. Lett. 1980, 45, 1597.
- (43) Bolwin, K.; Schnurnberger, W.; Schiller, G. Z. Phys. B: Condens. Matter 1988, 72, 203.
- (44) Wu, Q. H.; Liu, M.; Jaegerman, W. Mater. Lett. 2005, 59, 1480. (45) Jing, F. J.; Wang, L.; Liu, Y. W.; Fu, R. K. Y.; Zhao, X. B.; Shen,

R.; Huang, N.; Chu, P. K. Thin Solid Films 2006, 515, 1219.

- (46) Christie, A. B.; Sutherland, I.; Walls, J. M. Surf. Sci. 1983, 135, 225
- (47) Ison, V. V.; Rao, A. R.; Dutta, V. Solid State Sci. 2009, 11, 2003. (48) Baesman, S. M.; Bullen, T. D.; Dewald, J.; Zhang, D.; Curran, S.;
- Islam, F. S.; Beveridge, T. J.; Oremland, R. S. Appl. Environ. Microbiol.
- 2007, 73, 2135. (49) Hoang, D. L.; Dittmar, A.; Schneider, M.; Trunschke, A.; Lieske,
- H.; Brzezinka, K. W.; Witke, K. Thermochim. Acta 2003, 400, 153.
- (50) Belliere, V.; Joorst, G.; Stephan, O.; de Groot, F. M. F.; Weckhuysen, B. M. J. Phys. Chem. B 2006, 110, 9984.
- (51) Scheithauer, M.; Knozinger, H.; Vannice, M. A. J. Catal. 1998, 178, 701.
 - (52) Chan, S. S.; Bell, A. T. J. Catal. 1984, 89, 433.
- (53) Fuentes, A. F.; Reyna, E. R.; González, L. G. M.; Maczka, M.; Hanuza, J.; Amador, U. Solid State Ionics 2006, 177, 1869.
- (54) Cornaglia, L. M.; Munera, J.; Irusta, S.; Lombardo, E. A. Appl. Catal., A 2004, 263, 91.
- (55) Komatsu, T.; Kim, H. G.; Mohri, H. J. Mater. Sci. Lett. 1996, 15, 2026.
- (56) Xi, G.; Wang, C.; Wang, X.; Qian, Y.; Xiao, H. J. Phys. Chem. C 2008, 112, 965.
 - (57) Moskovits, M. Rev. Mod. Phys. 1985, 57, 783.
- (58) Chang, R. K.; Furtak, T. E. Surface Enhanced Raman Scattering; Plenum Press: New York, 1982.
- (59) Chourpa, I.; Lei, F. H.; Dubois, P.; Manfait, M.; Sockalingum, G. D. Chem. Soc. Rev. 2008, 37, 993.
- (60) Pieczonka, N. P. W.; Aroca, R. F. Chem. Soc. Rev. 2008, 37, 946. (61) Camden, J. P.; Dieringer, J. A.; Zhao, J.; Van Duyne, R. P. Acc. Chem. Res. 2008, 41, 1653.
 - (62) Nie, S.; Emory, S. R. Science 1997, 275, 1102.
- (63) Kneipp, K.; Wang, Y.; Kneipp, H.; Perelman, L. T.; Itzkan, I.;
- Dasari, R. R.; Feld, M. S. Phys. Rev. Lett. 1997, 78, 1667.
- (64) Campion, A.; Kambhampati, P. Chem. Soc. Rev. 1998, 27, 241. (65) Jana, S.; Pande, S.; Sinha, A. K.; Sarkar, S.; Pradhan, M.; Basu,
- M.; Saha, S.; Pal, T. J. Phys. Chem. C 2009, 113, 1386.
- (66) Galopin, E.; Barbillat, J.; Coffinier, Y.; Szunerits, S.; Patriarche, G.; Boukherroub, R. Appl. Mater. Interfaces 2009, 1, 1396.
 - (67) Miranda, M. M. Colloids Surf., A 2003, 217, 185.
 - (68) Karthikeyan, B. J. Sol-Gel Sci. Technol. 2008, 45, 79.
 - (69) Lin, Z. H.; Chang, H. T. Langmuir 2008, 24, 365.
 - (70) Hao, E.; Schatz, G. C. J. Chem. Phys. 2004, 120, 357.
 - (71) Tao, A. R.; Yang, P. D. J. Phys. Chem. B 2005, 109, 15687.

(72) Kang, T.; Yoon, I.; Jeon, K. S.; Choi, W.; Lee, Y.; Seo, K.; Yao, Y.; Park, Q. H.; Ihee, H.; Suh, Y. D.; Kim, B. J. Phys. Chem. C 2009, 113, 7492.

JP911658K