Photolytic preparation of tellurium nanorods†

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Well-defined tellurium nanorods have been prepared by the photolysis of $^t\mathrm{Bu}_2\mathrm{Te}_2$ in an aqueous micellar system incorporating dodecanethiol as an auxiliary morphology-directing agent.

Elemental tellurium has long been of interest because it is a p-type semiconductor ($E_g \approx 0.35$ eV) with many technologically useful properties, such as photoconductivity, piezoelectricity, and thermoelectricity.[1] Moreover, tellurium can be used as a starting material for the preparation of semiconductor tellurides (*e.g.*, PbTe,[2] CdTe,[2] Ag_2Te[3] and Bi_2Te_3[4]), and as a sacrificial reductive template for the formation of noble metals.[5] The crystal structure of trigonal tellurium (*t*-Te) is composed of helical chains of Te atoms that typically leads to anisotropic growth, and as a result, 1-D nanorods, nanowires, and nanotubes have been successfully prepared *via* chemical reductive routes,[6] or by the disproportionation of tellurite.[7] For example, Qian and co-workers prepared well-defined Te nanorods (aspect ratio ≈ 21) by reducing ammonium sulfotellurate with sodium sulfite in the presence of a surfactant.[8] There is still much to be achieved, however, in terms of developing solution routes to 1-D tellurium nanostructures that do not rely upon chemical reductants, yet still impart a high level of morphological uniformity.

As part of our general investigation into the utility of dialkyl dichalcogenides as starting materials for the preparation of semiconductor nanocrystals,[9] we found di-*tert*-butyl ditelluride ($^t\mathrm{Bu}_2\mathrm{Te}_2$) to be a convenient precursor to Te nanorods upon photolytic decomposition in a micellar environment. Using a modified literature procedure,[10] $^t\mathrm{Bu}_2\mathrm{Te}_2$ was synthesized by the reaction of ^{t}BuLi with elemental Te, followed by aqueous quenching and oxidation in air (see ESI†). Sublimation of the crude product afforded a crystalline solid with excellent purity that is stable in the solid state for one year (at 8 °C in the dark). Di-*tert*-butyl ditelluride possesses UV absorption bands at *ca.* 195, 262, and 367 nm (see ESI†), making it well suited for photolytic decomposition at a wavelength of 254 nm. As such, the photolytic decomposition of $^t\mathrm{Bu}_2\mathrm{Te}_2$ (50.0 mg, 0.135 mmol) was performed at 254 nm in a micellar solution composed of 5.0 mL of a non-ionic surfactant (polyoxyethylene(12) tridecyl ether), 0.10 mL of dodecanethiol, and 50 mL of water. Tellurium formation occurred over a period of 12 h, resulting in a dark brown suspension that was stable in the aqueous micellar solution for a period of several weeks.

The high dispersibility of the resulting Te nanocrystals in water likely results from a double layer of amphiphilic surfactant molecules, or a double layer of an inner layer of dodecanethiol and an outer layer of surfactant. Acetone was used to successfully precipitate the nanocrystals from aqueous solution. Nanocrystal precipitation likely occurs by reduction of the hydrophobic effect (*i.e.*, the driving force for aggregation of amphiphilic molecules into micelles or double layers). Non-hydrogen bonded polar solvents are known to dissolve amphiphiles into a molecular rather than micellar or double layer form.[11] Thus, as acetone is added to the aqueous suspension, the double layer surrounding the nanocrystals is likely disrupted, thereby causing nanocrystal agglomeration and precipitation. Once precipitated, the nanocrystals may be completely redispersed in water with gentle agitation.

As a consequence of the low enthalpies of the Te–Te and Te–C bonds (*ca.* 149 and 195 kJ mol^{-1}, respectively),[12] visible light is able to cause homolytic bond cleavage in diorganoditellurides with the extrusion of elemental Te and organic by-products. The photolytic decomposition of organotellurium compounds has received some application in the production of Te and telluride thin films;[13] however, we believe this is the first example of a photolytic preparation of well-defined Te nanocrystals. To probe the decomposition kinetics of $^t\mathrm{Bu}_2\mathrm{Te}_2$ in the micellar solution, the intensity of the 262 nm $^t\mathrm{Bu}_2\mathrm{Te}_2$ UV band was monitored over the course of the reaction (Fig. 1). Aliquots of the aqueous micellar solution were taken from the reaction at regular time intervals and the Te nanorods were removed *via* precipitation and centrifugation before the solution was analyzed by UV-vis spectrophotometry.

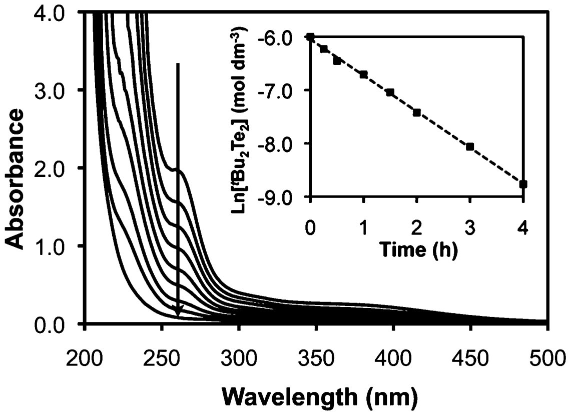

Fig. 1 Temporal change in the UV-vis spectrum of $^t\mathrm{Bu}_2\mathrm{Te}_2$ during the photolytic decomposition with 254 nm irradiation over 12 h. Apparent first-order reaction kinetics with respect to $^t\mathrm{Bu}_2\mathrm{Te}_2$ (inset).

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The photolytic decomposition of ${}^{t}Bu_2Te_2$ closely fits a first-order rate law with a rate constant $k = 0.68\ h^{-1}$ and a half-life $t_{1/2} = 1.0$ h under the conditions employed.

Transmission electron microscopy (TEM) revealed an anisotropic nanorod morphology for the resulting Te product (Fig. 2). The nanorods have an average diameter of 12.7 ± 3.0 nm and an average length of 46.5 ± 9.4 nm (aspect ratio $\approx$ 3.7). Although Te has a strong tendency toward anisotropic growth, it was determined that dodecanethiol is necessary for the growth of 1-D nanorods under these conditions. The photolytic decomposition of ${}^{t}Bu_2Te_2$ in the absence of dodecanethiol, but under otherwise identical conditions (*i.e.*, same concentration and photolysis time), yielded larger ellipsoidal Te nanocrystals with very low aspect ratios (~1.8, Fig. 2). The morphological change induced by dodecanethiol may be a result of the (001) face of Te not binding with the thiol as strongly as other faces. Alternatively, the thiol may bind to all exposed faces, impeding the accretion of Te atoms onto the growing nanorods, and giving thermodynamic control rather than kinetic control to Te deposition. The nanorods comprise lengthwise covalently bonded Te chains which are capped with the (001) crystal faces, whereas atoms deposited on the side faces are held together by weaker van der Waals attractions;[14] thus, a nanorod morphology might be expected from thermodynamic shape-control.

High-resolution TEM (HRTEM) analysis of the nanorods indicates growth along the [001] direction (or crystallographic *c*-direction) of the *t*-Te structure, as evidenced by the observation of (001) and (003) lattice planes normal to the growth direction (see ESI†). Moreover, HRTEM analysis suggests that the nanorods are single crystalline and without any appreciable amorphous shell. An HRTEM image (Fig. 2b) of an individual nanorod clearly shows distinct lattice spacings of 5.8 and 3.2 Å, which correspond to the (001) and (011) planes of *t*-Te, respectively. Powder X-ray diffraction (XRD) corroborates that the nanorods are phase pure *t*-Te (a = 4.46 Å; c = 5.91 Å), with no other crystalline impurities observed (Fig. 3). The calculated lattice parameters agree well with the literature values of a = 4.46 Å and c = 5.93 Å (JCPDS 04-007-5290). X-ray photoelectron spectroscopy (XPS) indicates that the nanorods are composed of elemental tellurium, with a Te $3d_{5/2}$ binding energy of 573.1 eV (see ESI†), which is in good agreement with literature values.[15] Furthermore, XPS analysis did not reveal the presence of a significant amount of oxidized Te^{4+} species, suggesting that the Te nanorods are stable under the experimental conditions described.

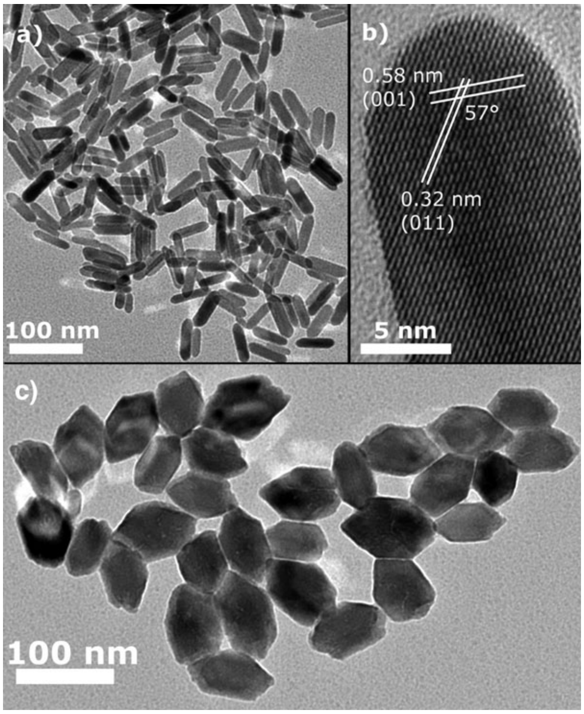

Fig. 2 TEM images of Te nanorods at (a) low and (b) high resolution. The high resolution image clearly shows the (001) lattice planes lying normal to the nanorod growth direction. (c) TEM image of the ellipsoidal Te nanocrystals formed without the addition of dodecanethiol.

UV-vis absorption spectra were obtained for the aqueous micellar dispersion of the Te nanorods (see ESI†). The spectrum revealed two distinct absorption bands with λ_{max} = 294 and 402 nm, and featureless control spectra of the micelles after tellurium precipitation (see ESI†) prove that the observed absorption bands are a result of the Te nanostructures. Previous studies have assigned these two distinct absorptions to band transitions between p-bonding → p-antibonding bands (270 nm), and between p-lone-pair → p-antibonding bands (617 nm).[16] Similar absorption bands have also been observed for Te thin films (*i.e.*, 270 and 561 nm).[17] It is possible that the blue shift observed for the low energy band relative to literature values is a result of the small diameter and/or elongated morphology; however, quantum confinement effects in Te nanocrystals have not been studied and further studies are warranted to explain the energy shift of this band. The ellipsoidal nanocrystals formed in the absence of dodecanethiol only show a single absorption band (λ_{max} = 352 nm) in the UV-vis spectrum, again suggesting that the electronic transitions in Te nanostructures are sensitive to their morphological properties.

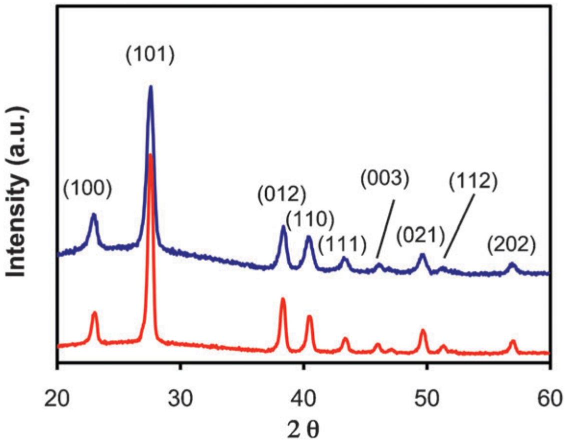

Fig. 3 XRD pattern of the nanorods (blue) and ellipsoidal nanocrystals (red) indexed to the trigonal phase of tellurium.

In summary, we have presented a novel photolytic preparation of well-defined *t*-Te nanorods. The synthesis is based on the facile photolytic decomposition of $^{t}Bu_2Te_2$, which produces elemental Te without the use of chemical reductants. Moreover, control over the nanorod morphology was rendered possible by addition of dodecanethiol to the aqueous micellar system. The resulting nanorods are expected to be useful morphology-directing synthons for a number of 1-D semiconductor tellurides.

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