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Synthesis of Tellurium Heterostructures by Galvanic Displacement Reaction of Zinc in Alkaline Baths

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ABSTRACT

Tellurium (Te) nanostructures, including nanowires and branched nanorods, were synthesized by galvanic displacement reaction (GDR) of zinc foils in alkaline baths containing TeO_3^{2-} ions. The dimension, morphology, and crystal structure of the Te nanostructures were controlled by varying the electrolyte composition, pH, and the reaction temperature. For examples, single crystalline Te nanowires were synthesized at low TeO_3^{2-} concentrations (e.g., 2 mM), whereas 3-D branched nanorods were obtained at higher TeO_3^{2-} concentrations (e.g., >10 mM) at a fixed pH of 13.1. The diameter of the branches was increased by increasing TeO_3^{2-} concentration. Solution pH also effected the morphology of Te heterostructures where the pH range from 12.8 to 13.1 yielded branched nanorods whereas higher pH (i.e., 14.7) yielded nanowires at a fixed TeO_3^{2-} concentration (i.e., 10 mM). Reaction temperature predominately effected on the dimension where the average diameter increased from 49 nm to 200 nm with increasing temperature from 4 °C to 50 °C. Various electrochemical analytical methods including open circuit potential (OCP), linear sweep voltammograms (LSVs) as well as linear potentiodynamic polarizations (LPs) were carried out to understand the underlying reaction mechanism. Based on these analysis, the formation of branched nanorods was attributed to secondary nucleation at the crystal imperfections.

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1. INTRODUCTION

Considerable attention has been directed towards various nanomaterials with controlled morphology and dimensions to tune their unique size and shape-dependent properties.[1] The ability to adjust the morphology, dimension and crystal structure of these nanomaterials is essential to optimize their electrical, thermal, photoconductive and mechanical behavior, in order to satisfy different applications.[2,3] For examples, reducing the diameter of one-dimensional (1-D) nanowires can enhance the materials' piezoelectric effect due to the flexoelectric effect [4–6]; engineering the nanomaterials to be three dimensional (3-D) can improve the light coupling into solar cells, since a refractive index gradient can be estibished [7–9]; and lowering the nanomaterials' dimension can enhance the thermoelectric properties owing to the quantum confinement and the stronger phonon scattering effects. [10]

Trigonal-Tellurium (t-Te) is a p-type semiconductor with a narrow band-gap energy of 0.35 eV at room temperature. Its hexagonal crystal structure contains six spiral chains at each corner and one in the center, which are bound together via van der Waals forces[11]. Because of its anisotropic crystalline structure [11], Te has a strong tendency to grow along the c-axis into 1-D structures without any additional physical templates. Owing to its unique crystal structure, it exhibits many unique physical properties including high photoconductivity, piezoelectric effect, and catalytic activity.[4,12–15]

Different morphologies of 1-D Te nanostructures including nanowires, nanoribbons, nanobelts, and nanotubes have been synthesized by various methods including vapor deposition [16–24]; hydrothermal[25–38], solvothermal[39–42], and polyol processes[43–45]; ultrasonic[46], microwave[47], photothermal [48], surfactant[49–51] and biomolecule-assisted methods[29]; as well as amino acids[52] and gluconate[53] controlled methods. However, few works have been reported on the synthesis of 3-D Te

nanostructures [41,54] and these reported methods generally require high operating temperature and pressure which limit its scalability and manufacturability.

Galvanic displacement reaction (GDR) is an electrochemical process driven by the difference in redox potentials between the solid substrate and the ions of the source materials, leading to deposition of the more noble material at the expense of the dissolution of the less noble material. Due to the ease of fabrication, GDR is an intriguing method to create various nanostructures with controllable morphology and dimensions. So far, synthesis of Te nanostructures by GDR have been reported with various nanostructures such as nanotubes[55], nanofibers [56], and nanowires.[57] Because of the low solubility of Te(IV) in a natural solution (1.6×10^{-4} g/L at pH of 7.0)[58], most syntheses were conducted in very acidic baths (pH close to zero)[15,55–61], in which the Te(IV) concentration can be increased (1.6 g/L at pH of zero). [58] However, low solution pH may accelerate the dissolution rate of synthesized materials and promote secondary reactions (*e.g.*, hydrogen gas evolution reaction (HER)) to lower the reaction efficiency. In contrast, Te(IV) dissolves readily in an alkaline bath with a solubility of 87.8 g/L at pH of 10.5 which is 55 fold greater than that at pH of zero. The higher solubility of Te (IV) in alkaline baths augments the deposition range providing greater flexibility to control the deposit's morphology.

In this work, Te nanostructures with varying size and shape were synthesized by galvanic displacement reaction in alkaline baths. Zinc was selected as a sacrificial material for three reasons:

the low redox potential of the Zn/ZnO_2^{2-}, its ability to form soluble products (*i.e.*, ZnO_2^-) in alkaline baths, and low rare material cost. The effects of TeO_3^{2-} concentration, pH, and reaction temperature of the electrolyte on the morphology, dimension and crystal structure of the resulting Te nanostructures were systematically studied. The underlying reaction mechanism of the GDR was investigated by several electrochemical analysis methods including OCP, LSV, and LP. The probable mechanism for the formation of branched Te nanostructures was proposed.

2. EXPERIMENTAL SECTION

The GDR electrolytes were prepared by dissolving various amount of tellurium dioxide (TeO_2, 99 + %, Acros Organics) in sodium hydroxide solutions (NaOH, 10 N, Fisher Chemical). High purity zinc foils (Zn, 0.25 mm thick, 99.98%, Alfa Aesar, Inc.) were cut into squares 0.8 cm on edge and used as the sacrificial material. These foils were degreased with detergents then sequentially rinsed three times in nanopure water and acetone (Fisher Chemical), and finally air dried before use. A Teflon cell with a gasket and an open area of $0.272 \, cm^2$ was used as the reactor for all of the GDRs. The Zn foils were sandwiched between the gasket and the Teflon sides, which were held together with screws to prevent any leakage. The GDRs were carried out by adding 0.5 mL of electrolyte into the open area of the cell in contact with the Zn foil. The reaction was allowed to proceed for 30 minutes without disturbance. Once the reaction was completed, the electrolyte was
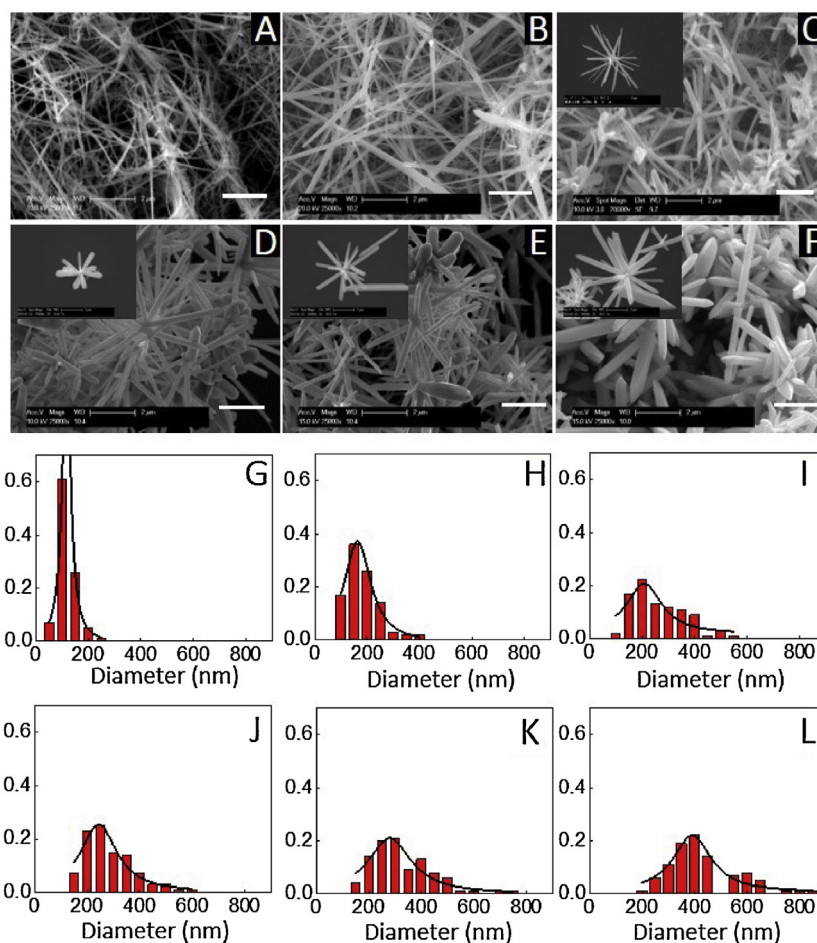

Fig. 1. SEM images of the Te nanostructures synthesized at (A) 2 mM, (B) 3 mM, (C) 10 mM, (D) 50 mM, (E) 100 mM, and (F) 550 mM TeO_3^{2-}, with a fixed pH of 13.1 and at 23 °C for 30 min. Diameter distributions of the Te nanostructures at (G) 2 mM, (H) 3 mM, (I) 10 mM, (J) 50 mM, (K) 100 mM, and (L) 550 mM TeO_3^{2-}. The black curves in the distribution plots are Lorentz fittings. All scale bars in A–F are 2 μm. The inserted images in C–F are the SEM images of the dispersed samples, correspondingly.