

Large-scale synthesis of Tellurium nanostructures via galvanic displacement of metals

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Abstract. Tellurium (Te) is an attractive semiconductor material for a wide range of applications in various functional devices including, radiation dosimeters, optical storage materials, thermoelectric or piezoelectric generators. In this work, large scale synthesis of tellurium (Te) nanostructures have been successfully carried out in different concentrations of aqueous solutions containing TeO₂ and NaOH, by galvanic displacements of Zn and Al which served as the sacrificial materials. Galvanic displacement process is cost-effective and it requires no template or surfactant for the synthesis of nanostructures. By varying the concentrations of TeO₂ and NaOH, etching temperatures and etching times, Te nanostructures of various forms of nanostructures were successfully obtained, ranging from one-dimensional needles and rod-like structures to more complex hierarchical structures. Microscopy examinations on the nanostructures obtained have shown that both the diameters and lengths of the Te nanostructures increased with increasing etching temperature and etching time.

1. Introduction

Functional nanostructures are critical to the ever-increasing complexity of technologies due to their capabilities in achieving the desired materials properties and functions for the state-of-art performances. It is important to have a cost-effective materials processing technique that produces nanostructures in large quantity with reproducible structures and properties to make them commercially viable and competitive. Trigonal-Tellurium (t-Te), for example, is a useful p-type semiconductor material with narrow bandgap of 0.35 eV at room temperature. It has been used in various technological applications due to its unique physical and chemical properties such as piezoelectricity, thermoelectricity, photoconductivity and photoelectricity [1]. It is a good candidate material for sensors, radiation dosimeters, optical storage materials, thermoelectric or piezoelectric generators. Te nanowires have been synthesized by thermal evaporation of Te powders [2], laser ablation [3], direct thermal oxidation at ambient pressure in a flow of O₂ without catalyst [4], hydrolysis of tellurium isopropoxide in the presence of tetra alkyl ammonium bromide solution [5], sol-gel process [6] and hydrothermal techniques [7]. These methods usually involve high temperature or pressure that limits their manufacturability and scalability. Nevertheless, reports on the large-scale synthesis of Te nanostructures, in particular, the formation of one-dimensional (1-D) Te



nanostructures by galvanic displacement (GD) have rarely been reported in spite of their wide applications.

We present, here in, an account of the large-scale synthesis of Te nanostructures via the process of galvanic displacements on commercially available zinc and aluminum foils as the sacrificial substrates. The method is facile, allows the use of flexible substrates and requires no template or surfactant. The effects of electrolyte concentration, reaction time and temperature on the morphology, dimension and crystallinity on the Te nanowires obtained were systematically analyzed to gain an insight into the growth mechanisms involved. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) were used to characterize the microstructures, morphologies, phases and dimensionalities of the nanostructures obtained.

2. Materials and Methodology

Commercially available Zn and Al foils were cut into sizes measuring approximately 1 x 1 cm, chemically cleaned using standard procedures and dried in an oven. The substrates were then immersed into an alkaline Te bath containing 0.5 ml aqueous solution of x mM TeO_2 and 1 M NaOH in a Teflon beaker. The composition of the x mM TeO_2 was systematically varied between x = 1, 10, 100 mM and the reaction times for etching ranged between 30 - 60 minutes with the etching temperatures varied from room temperature (RT) to 50°C. The as-prepared samples obtained were subsequently centrifuged for about 3 minutes before soaking in 0.5 ml of 1 M H_2SO_4 and rinsing thoroughly with DI water to reveal the Te nanostructures. The nanostructures were characterized by using an XRD (PANalytical XPert Pro MPD) and SEM (FEI QUANTA 400).

3. Results and Discussion

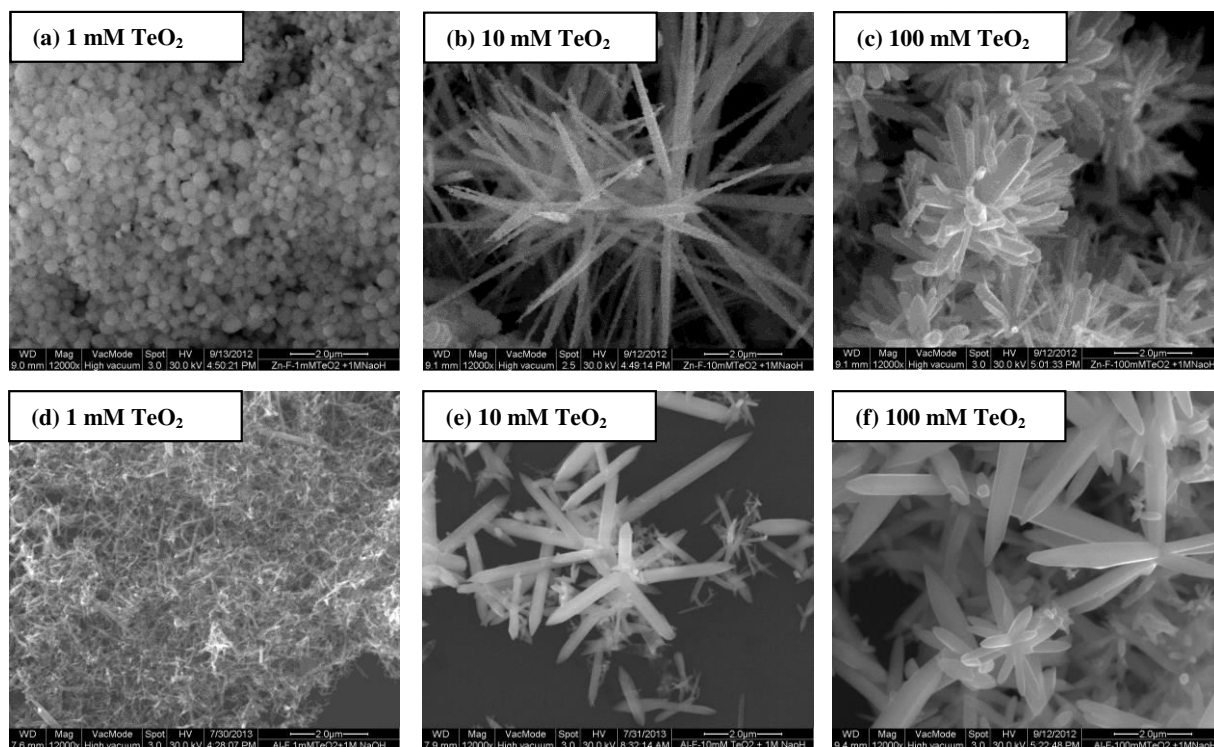


Figure 1. Te nanostructures formed from: (a-c) Zn and (d-f) Al substrates in electrolytes containing different concentrations of TeO_2 and 1 M NaOH at room temperature for 30 min.

The SEM micrographs in figure 1 reveal the various nanostructures of Te formed using different concentrations of TeO_2 with Zn and Al as the sacrificial materials respectively. The Te nanostructures formed exhibited different morphologies; (a) uniform granular structure, (b) pine leave structure of high aspect ratios with needle-shaped tips, (c) nanoflower structure, (d) nanofiber-like structure, (e) pine leave structure with pencil-shaped tips and (f) micron-sized pine leave structures with pencil-shaped tips. Lower tellurium ion concentrations (1 mM) were found to favor the kinetically-controlled 1-D nanostructures while higher tellurium ion concentrations favored the hierarchically-branched structures. More uniform nanostructures were obtained from the Zn substrates.

As shown in the SEM micrographs in figure 2, finer Te nanostructures were more apparent at higher reaction temperatures. With increasing reaction times for etching, the diameters of the nanostructures formed increase from 150 to 350 nm while their lengths increase steadily from 2 to 15 μm .

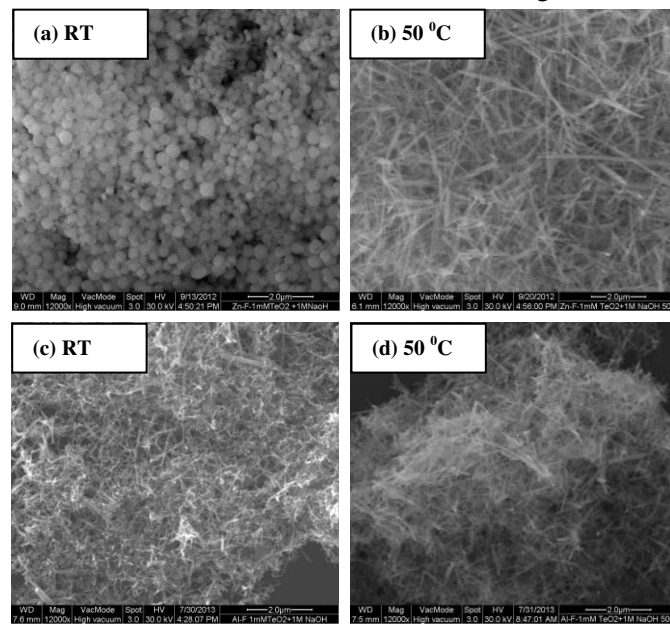


Figure 2. The effects of reaction temperatures on the Te nanostructures formed when (a-b) Zn and (c-d) Al substrates were etched for 30 min in 1 mM TeO_2 and 1 M NaOH.

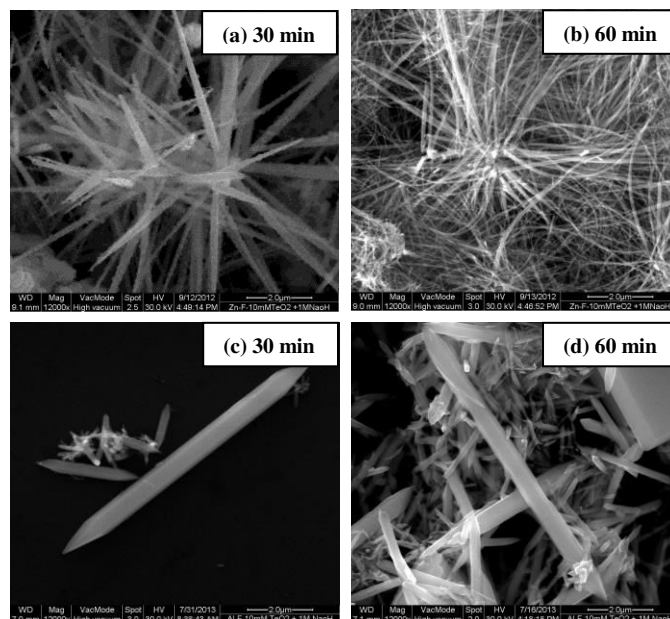


Figure 3. Effect of reaction time on the Te nanostructures synthesized from Zn (a-b) and Al substrates (c-d) in 10 mM TeO_2 and 1 M NaOH at room temperature.

In figure 4, the X-ray diffractogram for the Te nanostructures obtained from 1 mM TeO_2 and 1 M NaOH at room temperature on Zn showed no prominent diffraction peak which is indicative of the amorphous phase of Te. In contrast, the Te nanostructures obtained from 10 mM TeO_2 and 1 M NaOH on Al at room temperature are crystalline with all peaks indexed to the space group P3121 (152) hexagonal crystal structure of Te (the corresponding SEM micrographs are shown in Figs. 1 (e) and 3 (c)).

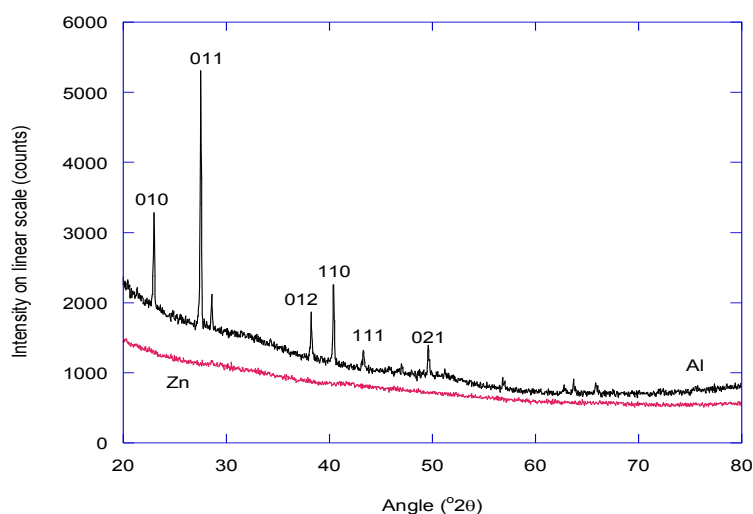


Figure 4. X-ray diffractograms of the Te nanostructures synthesized using: (bottom) 1 mM TeO_2 , 1 M NaOH and Zn substrate and (top) 10 mM TeO_2 and 1 M NaOH and Al substrate, both at room temperature

In general, the growth mechanisms for the nanostructures involved basically simple redox reactions where zinc and aluminum were oxidized while Te ions were reduced as shown in Fig. 5. Zn or Al provided the negative redox potentials to reduce the TeO_3^{2-} ions to Te (0) nanostructures on the surface of the metal foil [8]. This generated an electric current to support the continued growth of Te, yielding Te hierarchical structures, such as nanoflowers or pine leaf structures, depending on the growth conditions used. Different electrolyte concentrations affected the potential difference and current directionality, resulting in the formation of the Te nanostructures with different morphologies and large variations in length and diameter of the nanostructures. Galvanic displacement (GD) is a spontaneous electrochemical reaction driven by the difference in the redox potential between a solid substrate and the ions of a source material, leading to the deposition of a more noble material at the expense of a less noble material [9]. Since in a GD reaction, the substrate acts as the reducing agent, the synthesized product is of high purity. Besides capable of producing materials in large quantity, another advantage of GD is that it does not require any electrical connection. In this way, materials can be grown or deposited on any isolate part in a system.

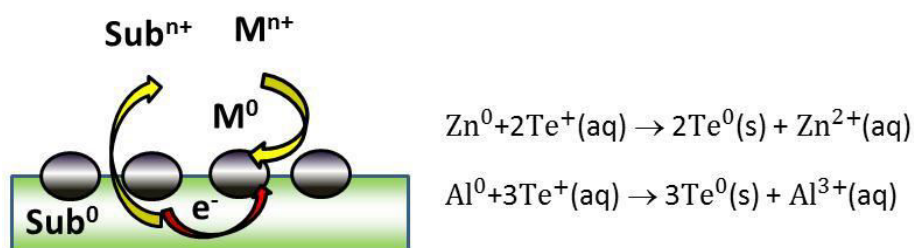


Figure 5. Schematics showing the reaction paths involved in a galvanic displacement reaction of Zn and Al.

4. Conclusion

The present study has successfully demonstrated the large-scale formation of Te nanostructures ranging from 1-D nanostructures to hierarchical branched structures via galvanic displacement. The morphologies of the Te nanostructures could be precisely tuned by adjusting the electrolyte concentration, etching temperature and etching time. This ability to tune the morphologies with different growth parameters is critical for achieving optimum Te nanostructures. In the formation of uniform and finer Te nanostructures, Zn acted as a better candidate material for galvanic displacement reactions compared to Al.

5. References

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