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Self-assembly of nanoparticles to form tree-like tellurium nanostructures using novel starting reagents

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ABSTRACT

A new rapid and single step thermal method was successfully developed to synthesize tree-like tellurium (Te) nanostructures at mild condition. Te nanostructures were synthesized using tellurium tetrachloride ($TeCl_4$) as a Te precursor and thioglycolic acid (TGA) as reducing and caping agent. No secondary chemical reducing agent is required to proceed and complete the reaction. A preliminary study on the possibility of developing a solar cell having the fluorine-doped tin oxide (FTO)/TiO_2/Te/Pt–FTO structure was also investigated to produce an inexpensive solar cell by Te nanostructures.

1. Introduction

As a p-type semiconductor with a direct band gap energy of 0.35 eV at room temperature, tellurium exhibits a wealth of unique properties, such as photoconductivity, nonlinear optical response, thermoelectric, catalytic activity, and strong piezoelectric effect and therefore its thin film and single crystal have wide applications in gas sensors, optoelectronic devices, nonlinear optical response devices, thermoelectric devices, piezoelectric devices, photonic crystal, self-developing holographic recording devices, radiative cooling devices, field-effect devices, and infrared acousto-optic deflector [1–4]. Therefore many investigations have been employed for this substance and various Te nanostructures such as nanotubes [5], nanowires [6] and nanorods [1] were prepared. Different chemical methods such as hydrothermal methods [6], microwave-assisted synthesis [7], and electrodeposition [8] have been used to prepare this material. Therefore, finding a new efficient, simpler method and a milder condition for preparation of Te nanostructures still is one of the most challenging issues. In this paper, we are going to report a simple, novel and rapid thermal procedure to synthesize tree-like Te nanostructures in an aqueous solution by employing $TeCl_4$ as a Te precursor and TGA as reductant and stability agent. Thioglycolic acid as a 'soft template' controls the morphology and plays a significant role in formation of nanostructures [9]. It can prevent Te nanocrystal aggregation and, in suitable conditions, can form a complex with Te^{4+} that turns to Te clusters. To our knowledge, it is the first time that $TeCl_4$ was used as tellurium source for the synthesis of Te nanostructures. A preliminary study on the possibility of developing a solar cell having the FTO/TiO_2/Te/Pt–FTO structure was also investigated.

2. Experimental

All the chemicals reagents were of analytical grade and were used as received without further purification. X-ray diffraction (XRD) patterns were recorded by a Philips-X'PertPro, X-ray diffractometer using Ni-filtered Cu Kα radiation at scan range of $10 < 2\theta < 80$. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. Transmission electron microscope (TEM) images were obtained on a Philips Zeiss-EM10C transmission electron microscope with an accelerating voltage of 80 kV. Sample for the TEM was prepared by ethanol, then placing a drop of this suspension onto a copper grid mesh of 300 coated with an amorphous carbon film, and then drying in air. The energy dispersive spectrometry (EDS) analysis was studied by XL30, Philips microscope. Room temperature photoluminescence (Pl) properties were studied on a Perkin-Elmer (LS 55) fluorescence spectrophotometer.

Synthesis of Te micro/nanostructures: In a typical experiment, 0.05 g $TeCl_4$, 15 ml distilled water and 15 ml thioglycolic acid were mixed in a beaker and magnetically stirred for 5 min. Then the mixture was heated to 80 °C at a rate of approximately 5 °C per minute and was maintained at the same temperature (80 °C) for 10 min before it was cooled down to room temperature by removing the heat source. The black obtained precipitates were centrifuged, washed with ethanol and distilled water several

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times. Finally, as obtain precipitates were dried at 60 °C for 10 h. Electrophoresis deposition (EPD) and doctor blade technique were utilized to the prepare TiO_2 and Te films [10,11]. To fabricate a FTO/TiO_2/Te/Pt–FTO solar cell, Te film was directly deposited on top of the TiO_2 (Scheme 1).

3. Results and discussion

Crystalline structure and phase purity of as-prepared products have been determined using XRD. The XRD pattern of as-prepared Te is shown in Fig. 1a. The diffraction peaks observed in Fig. 1a can be indexed to pure hexagonal phase of tellurium ($a=b=4.4572$ Å, $c=5.9290$ Å) with space group of P3121 and JCPDS no. 86-2268. No diffraction peaks from other species could be detected, which indicates the obtained sample is pure. From XRD data, the crystallite diameter (D_c) of tellurium nanostructures was calculated to be 24 nm using the Scherer equation. Chemical purity of product was examined by energy dispersive X-ray spectroscopy (EDX) (Fig. 1b), which indicates only Te peaks exist in the samples except the peak due to the use of a Au-coated substrate for samples examination. Different scales of SEM and TEM images were taken in order to characterize the morphology, size, and microstructure of the product (Fig. 2). It seems that the products are found to be tree-like self-assemblies Te nanostructures (Fig. 2a–c). According to the TEM images (Fig. 2d–h), products are composed of tree-like nanostructures, almost consistent with that observed from SEM images (the background phases in Fig. 2d–i are carbon-coated copper grid).

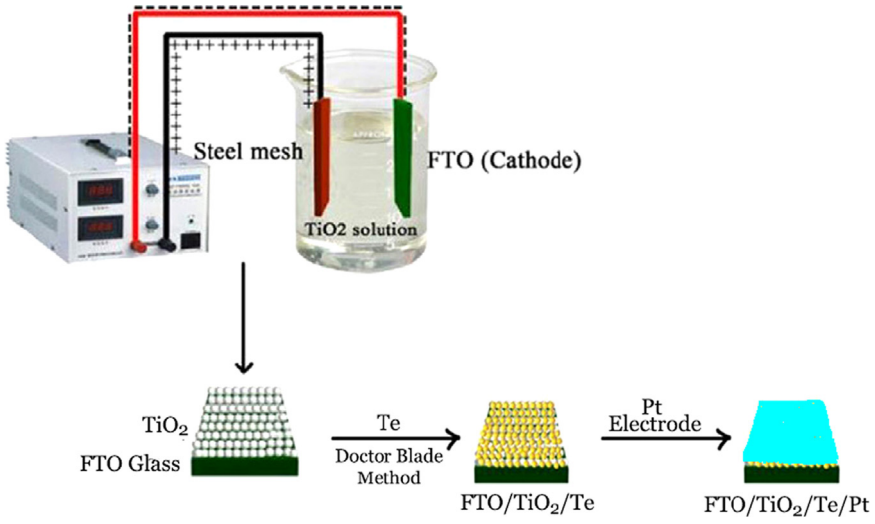
Fig. 2i shows the high-magnification TEM image of the product which clearly revealing that the Te tree-like nanostructure prepared by this method is consists of nanoparticles with average particle size ~10–25 nm.

In the process of the reaction, the selection of the Te source is critical, since the usual Te source (elemental tellurium) does not dissolve in distilled water, and this will lead to a heterogeneous reaction. $TeCl_4$ is a good tellurium source due to its solubility in distilled water. To the best of our knowledge, it is the first time that $TeCl_4$ was used as the Te source for the synthesis of Te. In our experiment, when $TeCl_4$ is added into the deionized water, a completely clear acidic solution was obtained that contains H_2TeO_3 (Eq. (1)); however, H_2TeO_3 can be quickly converted to Te by TGA upon heating (Eq. (2)). Thioglycolic acid has two functional groups –COOH, and –SH. When excess concentration of TGA was used, it absorbed on the surface of Te^{4+} and hydrogen and S–S bonds were formed between TGA molecules. The Te nanoparticles cross-link via hydrogen bonds and S–S bond interactions and finally turned to Te nanorods. $HSCH_2CO_2H$ (TGA) is easily oxidized to the corresponding disulfide $[SCH_2CO_2H]_2$. Therefore, the reactions in the thermal process can be described as follows:

$$TeCl_4 + 3H_2O \rightarrow H_2TeO_3 + 4HCl \quad (1)$$

$$4HSCH_2CO_2H + H_2TeO_3 \rightarrow [SCH_2CO_2H]_4 + Te + 3H_2O \quad (2)$$

Photoluminescence (PL) measurement of Te nanocrystals was carried out at room temperature with excitation wavelength 215 nm which are laid out in Fig. 3a. The spectrum has a emission



Scheme 1. The solar cell fabrication process.

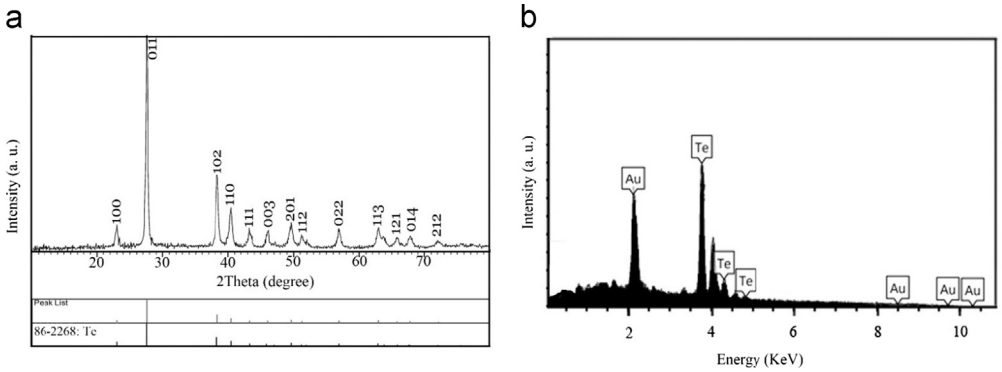


Fig. 1. a: XRD pattern of the as-synthesized Te and b: EDX analysis of Te nanostructures.