Microwave-polythiol Method. A New Route to Preparation of Tellurium with Various Morphologies

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A new microwave-polythiol method has been developed for preparation of tellurium (Te) with various morphologies. 1,2-Ethanedithiol (EDT) was used as both a reducing reagent and a solvent. Reduction of TeO_2 by EDT was achieved by microwave-heating at $\leq$140 °C for 30 min. The morphology of Te could be controlled by changing experimental parameters.

The polyol method was employed for the preparation of nanoparticles[1–6] in the past decade. In this method, a metal precursor and a high-boiling-point polyol that acts as both a reducing reagent and a solvent are used. Very recently, microwave was used in combination with the polyol method (microwave-polyol method) to prepare spherically shaped nanoparticles of Pt and Ag,[7] CdSe,[8] $Cd_{1-x}Zn_xSe$,[9] and TiO_2.[10] Microwave heating is promising because of its unique effects compared with the conventional heating, such as rapid volumetric heating, higher reaction rates and shorter reaction time, higher reaction selectivity, and energy saving.

In order to lower preparation temperature for nanostructures, we used a polythiol (1,2-ethanedithiol (EDT) in this study) as a reducing reagent and developed a new microwave-polythiol method. EDT has a boiling point of ca. 147 °C, much lower than that of its polyol counterpart (ethylene glycol (EG), boiling point ca. 197 °C). By using the microwave-polythiol method, we prepared successfully Te with various morphologies at relatively low temperatures ($\leq$140 °C) in a relatively short processing time (30 min).

In a typical experiment, a mixture of analytical grade TeO_2 and EDT was microwave-heated for 30 min. The microwave oven (2.45 GHz, maximum power 300 W) used for sample preparation was a focused single-mode microwave synthesis system (Discover, CEM, USA). The unique, circular single-mode cavity ensured that samples were in a homogenous highly dense microwave field. The system was equipped with an in situ magnetic stirring and a water-cooled condenser. Temperature was accurately controlled by automatic adjusting of microwave power. The X-ray powder diffraction (XRD) patterns were recorded using a Japan Rigaku D/max 2550 V X-ray diffractometer with high-intensity Cu Kα radiation (λ = 1.54178 Å) and a graphite monochromator. The TEM images were taken with a Hitachi JEM-200CX transmission electron microscope. Differential scanning calorimetric analysis (DSC) was carried out with a STA-409PC/4/H Luxx simultaneous TG-DTA/DSC apparatus (Germany) with a heating rate of 10 °C min^{-1} in a flowing high-purity N_2 gas.

Figure 1 shows XRD pattern of a typical sample prepared by microwave-heating of 0.16 g TeO_2 and 10 mL EDT at 140 °C for 30 min. The product was a single phase of well-crystallized elemental Te with a hexagonal structure. This indicates that EDT reduced TeO_2 to form Te at 140 °C. The sample prepared at a lower temperature (80 °C) has a similar XRD pattern as Figure 1, indicating the formation of Te even at a temperature as low as 80 °C. Our study showed that by using EG as a reducing reagent, TeO_2 could not be reduced by microwave-heating at temperatures lower than 180 °C. Therefore, the preparation temperature for Te from TeO_2 can be much lowered by using EDT instead of EG.

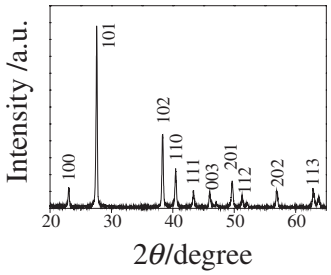

Figure 1. XRD pattern of a typical sample prepared by microwave-heating of 0.16 g TeO_2 and 10 mL EDT at 140 °C for 30 min.

The morphologies of samples were investigated with TEM. Figure 2 shows TEM micrographs of four samples. Figures 2a, 2b, and 2c show TEM micrographs for the same sample as in Figure 1, from which one can see the interesting morphologies of Te microstructures. These Te microstructures consist of nano- and microrods with diameters ranging from ca. 40 to ca. 500 nm and with lengths up to several μm. Each Te microstructure has the same common point, implying that crystal growth of rods started from the same common point. When TeO_2 was reduced by EDT at a lower temperature (80 °C), both spherical particles with diameters of several hundred nanometers and nanorods with diameters of ca. 20 to ca. 100 nm and with lengths of submicron to ca. 1 μm were observed, as shown in Figures 2d and 2e. The electron diffraction pattern of spherical particles (the inset in Figure 2d) shows that they were amorphous. However, nanorods were crystalline (the inset in Figure 2e).

When TeO_2 was reduced by a mixture of EDT and EG at 140 °C for 30 min, nano- and microrods with diameters ranging from ca. 80 to ca. 270 nm and with lengths up to ca. 2.5 μm were produced (Figure 2f). Electron diffraction pattern (the inset of Figure 2f) of a random chosen individual rod indicates that they were single-crystalline. Our study showed that EG could only reduce TeO_2 to form Te rods similar to those in Figure 2f at temperatures between ca. 180 and ca. 195 °C. However, by using a mixture of EDT and EG, the preparation temperature for Te rods can be lowered.

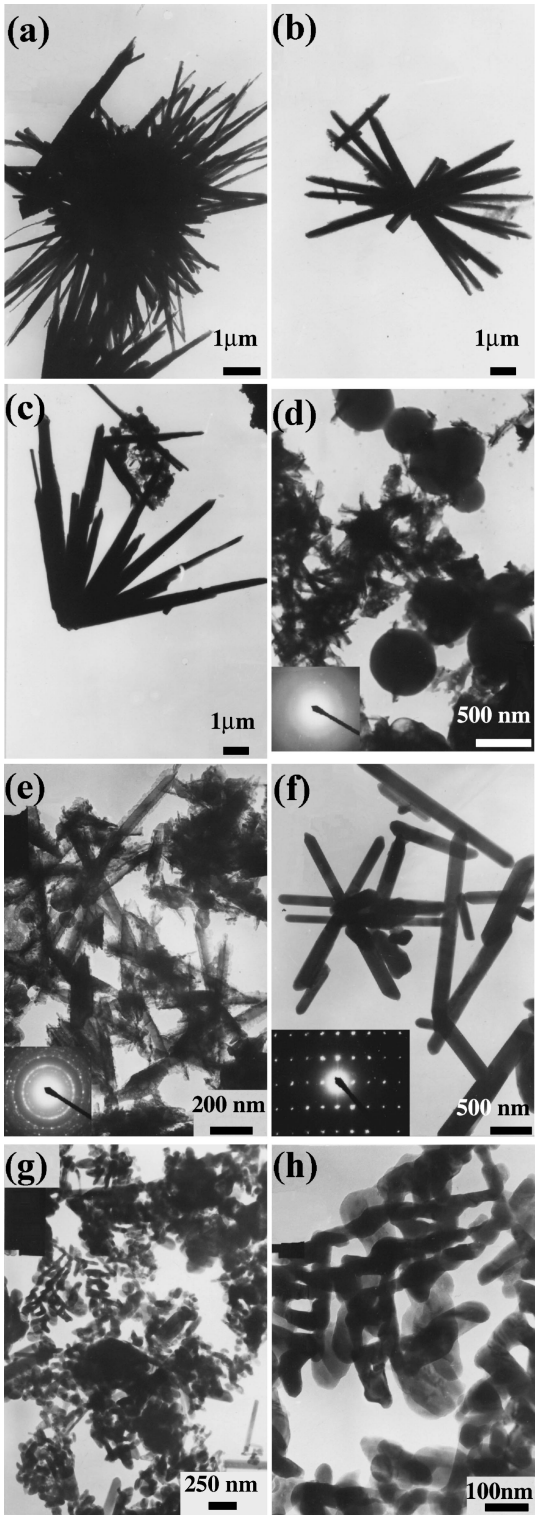

Figure 2. TEM micrographs of Te prepared by microwave-polythiol method. (a), (b) and (c) are for the same sample as in Figure 1; (d) and (e) are for sample prepared at 80 °C for 30 min; (f) is for sample prepared by microwave-heating of 0.16 g TeO_2 in 5 mL EDT and 5 mL EG at 140 °C for 30 min; (g) and (h) are for Te prepared by microwave-heating of 0.16 g TeO_2 in 5 mL EDT and 5 mL H_2O at 80 °C for 30 min.

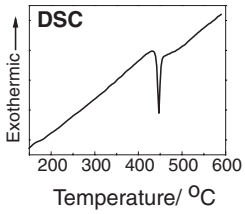

Figure 3. DSC curve of the same sample as in Figure 1.

We also explored the reduction of TeO_2 by a mixture of EDT and water microwave-heated at 80 °C for 30 min (Figures 2g and 2h). Three morphologies of Te were observed: spherical, rope-like and rod-like. Electron diffraction patterns show that Te with all three morphologies was crystalline. One can see that Te with various morphologies can be prepared by controlling experimental parameters. EDT may play a role (e.g. as a surface modifying reagent) in Te morphology control.

Figure 3 shows the DSC curve of the same sample as in Figure 1. The DSC curve shows an endothermic peak with an onset temperature of 441.5 °C and a maximum at 446.3 °C, corresponding to the melting of Te sample. This melting point is close to that of bulk Te (449.7 °C). Since the DSC measurement was performed in a flowing high-purity N_2 gas, no oxidation of Te was observed, as supported by the fact that no exothermic peak occurred in the DSC curve.

In summary, we have demonstrated successful preparation of Te with various morphologies by a new microwave-polythiol method at relatively low temperatures ($\leq$140 °C) in a relatively short processing time (30 min). We expect that this new method may also be employed to prepare many other kinds of nanostructures. The related research is in progress.

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