Hydrazine–Cadmium Tellurite Hybrid Microcrystals: An Efficient Precursor to Porous Cadmium Telluride and Tellurium Architectures Through Its Thermal Decomposition

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ABSTRACT

Well-defined platelet-like hydrazine–cadmium tellurite hybrid microcrystals have been synthesized by a solvothermal reaction of cadmium chloride, sodium tellurite, and hydrazine hydrate in a mixed solvent containing *n*-propylamine and deionized water. The formula of the hybrid platelet-like microcrystals has been proposed based on a combination of powder X-ray diffraction pattern (PXRD), elemental analysis, thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). Controlled thermal decomposition of this hybrid precursor can lead to the formation of porous platelet-like microarchitectures. Pure porous cadmium telluride architectures were obtained by using hydrochloric acid to dissolve CdTeO₃ remaining in the sample after thermal decomposition at 450 °C. In addition, unique nanoporous tellurium architectures were obtained by using hydrochloric acid to dissolve the amorphous Cd(N₂H₄)TeO₃ formed after thermal decomposition at 300 °C, followed by an *in situ* topotactic reaction between the residual three-dimensional (3-D) skeleton of cadmium telluride nanocrystallites and TeO₃²⁻. Brunauer–Emmett–Teller (BET) analysis and a study of the optical properties of these porous cadmium telluride and tellurium materials have also been carried out.

KEYWORDS

Thermal decomposition, hydrazine, hybrid, porous architecture, tellurium

Introduction

As novel materials combining two or more components, hybrid materials have been extensively studied in fundamental research and applied in industry in recent years [1]. For example, a variety of organoamine–metal chalcogenide organic–inorganic hybrid materials have been synthesized and shown to have novel optical, electrical, and thermal expansion properties [2–12]. In particular, various hydrazine-

based hybrid materials can be synthesized by using hydrazine as both solvent and reagent because of its high solubility and reducing capability toward chalcogenide elements. For example, Mitzi and his co-workers have reported a series of hydrazine-based hybrid materials including (N₂H₅)₄Sn₂S₆ [13], (N₂H₅)₄Ge₂Se₆ and (N₂H₄)₃(N₂H₅)₄Sn₂Se₆ [14], α - and β -(N₂H₄)₂ZnTe [15], and (N₂H₄)(N₂H₅)Cu₇S₄ [16]. Yuan et al. have also systematically investigated a series of structures of hydrazine-based metal chalcogenide

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hybrids spanning from zero-dimensional (0-D) discrete molecules, to 1-D chains, 2-D layers, and 3-D networks [17]. In addition, Li's group have reported a layered monohydrazine compound $\text{ZnTe}(\text{N}_2\text{H}_4)$ [4]. Recently, a new hydrazine–metal chalcogenide hybrid framework material, $\text{Mn}_2\text{SnS}_4(\text{N}_2\text{H}_4)_2$, in which the hydrazine acts as an integral part of the framework as opposed to being located in the pores, has been reported by Kanatzidis et al. [18].

Hydrazine-based hybrid materials can be used as efficient precursors for the fabrication of functional inorganic substrates, films, and devices by simply annealing to evaporate hydrazine, taking advantage of its low boiling point. In 2004 Mitzi et al. reported a technique for spin coating ultrathin (50 Å) crystalline and continuous metal chalcogenide films, based on the low-temperature decomposition of highly soluble hydrazinium precursors [13]. A series of related thin-film field-effect transistors (TFTs) have subsequently been fabricated using a similar strategy [19–21].

Moreover, mixed solvent systems have been demonstrated to be efficient media for the synthesis and controlled crystal growth of hybrid materials [22, 23], such as hybrid nanobelts [24], nanofibers [25], and nanoribbons [26]. These uniform nanostructured hybrid materials can be used as efficient precursors for fabricating pure inorganic nanostructured materials [25, 26].

Herein, we report a new approach for synthesizing hydrazine–cadmium tellurite hybrid microcrystals by a solvothermal reaction in a mixed solvent system and study their morphology evolution. These well-defined hydrazine–cadmium tellurite hybrid microcrystals can act as efficient precursors for the fabrication of porous semiconducting cadmium telluride and nanoporous tellurium architectures. The resulting porous cadmium telluride and tellurium not only retained similar external morphology on a micrometer or larger scale, but also displayed tailored internal nanostructures.

1. Experimental

Sodium tellurite (99%), cadmium chloride hemidi-hydrate (99%), hydrazine hydrate solution (85 wt.%), *n*-propylamine (98%), and hydrochloric acid (37 wt.%) were all purchased from Shanghai Chemical Reagents

Co. Ltd. All chemicals were used directly as received without any purification.

1.1 Hydrazine–cadmium tellurite hybrid microcrystals grown in a mixed solvent system

Typically, 0.5 mmol of sodium tellurite, 0.5 mmol of cadmium chloride hemidi-hydrate, 6 mL of *n*-propylamine, 3 mL of deionized water, and 2 mL of hydrazine hydrate were added to a Teflon-lined autoclave with a capacity of 23 mL. The mixture was vigorously stirred magnetically for 10 min to form a homogeneous suspension. The autoclave was then sealed and heated at 100 °C for a certain period. After being cooled to room temperature, the grey powder was collected by centrifugation and washed three times each with ethanol and then distilled water. The final product was dried at 50 °C in a vacuum oven.

1.2 Fabrication of porous cadmium telluride architecture

Typically, 0.1 g of uniform hydrazine–cadmium tellurite hybrid microcrystals was transferred into a porcelain boat. The boat was put into a tube furnace and heated to 450 °C and kept for 2 h under a nitrogen atmosphere. After being cooled to room temperature naturally, the brown product was collected. This material was then added to 40 mL of 0.1 mol/L HCl solution and the mixture stirred for 10 min. The resulting black powder was collected by centrifugation and washed three times each with deionized water and ethanol and finally dried at 50 °C in a vacuum oven. The mass of the final product was 0.0256 g, corresponding to a yield of cadmium telluride of 51.30 wt.%.

1.3 Fabrication of porous tellurium architecture

Typically, 0.1 g of uniform hydrazine–cadmium tellurite hybrid microcrystals was transferred into a porcelain boat. The boat was put into a tube furnace and heated to 300 °C and kept for 2 h under a nitrogen atmosphere. After being cooled to room temperature naturally, the brown product was collected. This material was then added to 40 mL of 0.1 mol/L HCl solution and the mixture stirred for 10 min. The resulting black powder was collected by centrifugation and washed three times each with deionized water and ethanol

and finally dried at 50 °C in a vacuum oven. The mass of the final product was 0.0176 g, corresponding to a yield of tellurium of 44.22 wt.%.

1.4 Characterization

The phases of the as-prepared products were determined by powder X-ray diffraction (PXRD) using a Philips X'Pert Pro Super X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). Transmission electron microscopy (TEM) images were recorded with a Hitachi H-7650 transmission electron microscope at an acceleration voltage of 120 kV. Scanning electron microscopy (SEM) images were taken with a Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV. Thermal gravimetric analysis (TGA) was carried out with a Shimadzu DTG-60H thermal analyzer, with a heating rate of 10 °C/min and an N₂ flow of 50 mL/min. UV–visible spectra of the solid samples were recorded on a Shimadzu DUV-3700 spectrometer. Brunauer–Emmett–Teller (BET) analysis was carried out on a Micromeritics ASAP 2020 M + C instrument. The inorganic elements were determined by inductively coupled plasma atomic emission spectroscopy (ICP–AES). The composition of N, C, and H was determined using an Elementar Vario EL III analyzer.

2. Results and discussion

2.1 Synthesis and formula determination of the hydrazine–cadmium tellurite hybrid microcrystals

Hydrazine–cadmium tellurite hybrid microcrystals were obtained from a solvothermal reaction. The PXRD pattern of the product is shown in Fig. 1(a). There is no matching PXRD pattern in the powder diffraction file (PDF) database of the International Centre for Diffraction Data (ICDD), which indicates that this hybrid material is a totally new phase. The PXRD pattern was indexed by the semi-exhaustive trial-and-error powder indexing (TREOR) method using the program Powder X [27] which gave lattice parameters of $a = 7.97 \text{ \AA}$, $b = 9.32 \text{ \AA}$, $c = 7.78 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 97.25^\circ$, and $\gamma = 90^\circ$. The main indexed peaks

are marked in Fig. 1(a) and the indexing of the diffraction peaks is given in Table S-1 in the Electronic Supplementary Material (ESM).

Analysis of the PXRD pattern indicates that the product is possibly a hybrid material because of the large lattice parameters. In order to confirm the composition of the product, elemental analysis was carried out. The elements N, C, H, Cd, and Te in the sample were all detected but the amount of C was very small (0.35 wt.%), which indicates that the *n*-propylamine was only adsorbed on the surface of the sample instead of being incorporated into the hybrid structure. The sum of the mass percentages of N, H, Cd, and Te was only 85.07 wt.%. Furthermore, X-ray photoelectron spectroscopy (XPS) analysis indicated that the valence state of Te was mainly +4 (Fig. 1(b)). Hence, it can be concluded that oxygen was also present in the product. A possible formula for the product is Cd(N₂H₄)TeO₃, which is similar to our previously reported compounds of the type Cd(L)TeO₃ (L = a polyamine) [25]. The calculated mass percentages of N, H, Cd, and Te elements based on the proposed formula are given in Table 1 and are consistent with the experimental values. The following equation can be proposed for the thermal decomposition of Cd(N₂H₄)TeO₃:

The TGA results further support the proposed formula. Figure 1(c) shows that the measured mass loss on heating the product is 19.12 wt.%, which is consistent with the calculated mass loss for the above reaction of 19.99 wt.%. The phases present after the TGA experiment were identified as a mixture of CdTe and CdTeO₃ (Fig. 1(d)), which is also consistent with the proposed thermal decomposition process shown in Eq. (1).

Table 1 Elemental analysis results and the corresponding calculated values based on the proposed formula

Element	Cd	Te	N	H	C
Found (wt.%)	37.85	35.97	9.31	1.93	0.35
Calculated (wt.%)	35.12	39.86	8.75	1.25	0

Figure 1 (a) PXRD pattern of the product of the solvothermal reaction. The pattern was indexed by the TREOR method using the program Powder X and the main indexed peaks are marked. (b) XPS spectrum of the Te 3d region of the product of the solvothermal reaction. (c) TGA curve of the product of the solvothermal reaction. (d) PXRD pattern of the product after TGA (α represents peaks of CdTe, β represents peaks of CdTeO₃, and γ represents peaks of Te impurity)

2.2 Morphology evolution of Cd(N₂H₄)TeO₃ with increasing reaction time

SEM images of as-synthesized Cd(N₂H₄)TeO₃ hybrid microcrystals are shown in Fig. 2. The hybrid microcrystals have a uniform platelet morphology

with a mean lateral size of several micrometers.

The evolution of phases and morphologies of Cd(N₂H₄)TeO₃ hybrid microcrystals grown in the mixed solvent system were investigated by time-dependent experiments. Figure 3 shows the PXRD patterns of products obtained after different reaction times. The

Figure 2 SEM images of Cd(N₂H₄)TeO₃ hybrid microcrystals: (a) low magnification image and (b) higher magnification image

Figure 3 PXRD patterns of the product obtained in a mixed solvent system with different reaction time: (a) 12 h, (b) 2 days, (c) 5 days, and (d) 7 days. * denotes a Te phase

intensities of the diffraction peaks varied with reaction time, but the the main phases were always present. At the initial reaction stage, the intensity of the diffraction peaks was low (Fig. 3(a)), and became higher with increasing reaction time (Figs. 3(b) and 3(c)). However,

the peak intensities decreased again with very long reaction time and a small amount of a new phase, Te, was formed (Fig. 3(d)).

The variation in diffraction peak intensity is related to the evolution of morphology with reaction time. SEM images of the hybrid microcrystals produced at different reaction time are shown in Fig. 4. Platelet-like crystals were initially formed (Fig. 4(a)), and then other hybrid crystals grew on the surface of the initially formed platelet-like crystals when the reaction time was prolonged (Fig. 4(b)) and the crystallinity was further improved (which is consistent with the observed increase in the diffraction peak intensities). However, further increases in reaction time led to the collapse of the hybrid crystals (see the inset image in Fig. 4(c)), which can be attributed to the reaction of the hydrazine in the hybrid structure with the cadmium tellurite. Finally, the morphologies of the hybrid crystals evolved into the hierarchical structures shown in Fig. 4(d) as result of the collapse of the hybrid crystals due to the reaction between hydrazine and cadmium tellurite. The reduction in the intensity of the diffraction peaks of the hybrid phase and the appearance of new

Figure 4 SEM images of hybrid microcrystals formed after different reaction time: (a) 12 h, (b) 2 days, (c) 5 days, and (d) 7 days. The inset image in (c) shows the area where dissolution of the crystal is occurring

peaks corresponding to a Te phase (Fig. 3(d)) further confirmed the reaction between the hydrazine and cadmium tellurite at extended reaction times.

2.3 Fabrication of porous architectures by temperature-dependent thermal decomposition

As discussed above, the proposed stoichiometry of the hydrazine–cadmium tellurite hybrid microcrystals is $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$. TGA indicated a very rapid mass loss in the range 150–450 °C which can be attributed to the elimination of hydrazine. It should be very interesting to study the evolution of morphologies and phase transformations during the thermal decomposition process. Since hydrazine is a very volatile material and a strong reducing agent, its vaporization should lead to highly porous structures as has previously been reported when CO_2 gas was evolved [28, 29].

A systematic investigation of the thermal decomposition of $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ was carried out. The PXRD patterns of the thermal decomposition products obtained at different annealing temperatures are shown in Fig. 5. An almost amorphous phase of $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ was first formed (Fig. 5(a)) due to some elimination of hydrazine from the hybrid structure. Crystalline CdTe was then formed at higher thermal decomposition temperature (Fig. 5(b)), as a result of reduction by hydrazine. Thus, on increasing the thermal decomposition temperature, the almost amorphous $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ phase was transformed first to CdTeO_3 and finally a mixture of CdTe and CdTeO_3 was obtained (Fig. 5(e)); this is consistent with the proposed thermal decomposition process shown in Eq. (1). Figure 6 shows SEM images of thermal decomposition products obtained at different annealing temperatures. When the $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ platelet-like microcrystals were heated to 300 °C and kept at that temperature for 2 h, only a few pores appeared on the surfaces of the hybrid microcrystals (Fig. 6(a)). When the thermal decomposition temperature was increased to 350 °C, the morphologies changed relatively little, but more pores and cracks appeared on the surfaces (Fig. 6(b)).

A drastic morphology transformation occurred at 400 °C as shown in Fig. 6(c). The microcrystals became

Figure 5 PXRD patterns of the thermal decomposition products of $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ at different temperatures: (a) 200 °C, (b) 300 °C, (c) 350 °C, (d) 400 °C, and (e) 450 °C. (f) The PXRD pattern of porous CdTe architecture obtained by using hydrochloric acid to wash the sample obtained after thermal decomposition at 450 °C; the weak peak at ca. 23° is the (001) diffraction peak of wurtzite phase CdTe. # denotes amorphous $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$. * denotes CdTeO_3

porous and pores appeared inside the microcrystals (inset image in Fig. 6(c)). The PXRD pattern also displayed significant changes in that peaks from the almost amorphous $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ disappeared, but those from crystalline CdTeO_3 appeared (Fig. 5(d)). With a further increase in annealing temperature to 450 °C, the pores shrank and collapsed, resulting in the formation of porous structures (Fig. 6(d)). PXRD shows that these porous microcrystals were a mixture of CdTe and CdTeO_3 (Fig. 5(e)). Hydrochloric acid was introduced to dissolve the CdTeO_3 phase in the porous architectures, leading to pure porous CdTe (Fig. 5(f)). The resulting porous CdTe microcrystals still retained a platelet-like morphology as shown in Fig. 7.

2.4 Fabrication of porous tellurium architectures through hydrochloric acid leaching

Figure 5(b) shows that the hybrid $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ material was transformed to a mixture of a CdTe phase with low crystallinity and amorphous $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ after thermal decomposition at 300 °C. A dilute solution of hydrochloric acid was used to treat the thermally decomposed sample. Surprisingly,

Figure 6 SEM images of $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ hybrid microcrystals thermally decomposed at different temperatures: (a) 300 °C, (b) 350 °C, (c) 400 °C, and (d) 450 °C. The inset images in (c) and (d) are at higher magnification

Figure 7 SEM images of porous CdTe microcrystals obtained by using hydrochloric acid to wash the sample obtained by thermal decomposition of $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ at 450 °C: (a) low-magnification image and (b) higher-magnification image

the sample was converted to a pure tellurium phase (Fig. 8(a)) and pores were formed inside the microcrystals (Figs. 8(b) and 9). Both TEM and SEM images showed that the porous microcrystals retained the original platelet-like shape. The pores were homogeneously distributed throughout the microcrystals leading to a nanoporous architecture. To the best of our knowledge, this is the first report of the synthesis of self-supporting nanoporous tellurium microcrystals.

Interestingly, it was observed that subsequent washing with dilute hydrochloric acid for samples that had been thermally decomposed at different annealing temperatures afforded different phases and porous morphologies. When the hydrazine–cadmium tellurite hybrid microcrystals were annealed at 300 °C for 2 h, the material became amorphous because of elimination of hydrazine and poorly crystalline CdTe nanocrystals were formed by the action of hydrazine as a reducing agent (Fig. 5(b)).

Figure 8 (a) PXRD pattern and (b) TEM image of the material obtained after thermal decomposition of $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ at 300°C followed by treatment with dilute hydrochloric acid

Figure 9 SEM images of nanoporous tellurium architectures obtained after thermal decomposition of $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ at 300°C followed by treatment with dilute hydrochloric acid

The sample obtained after thermal decomposition was brown. After adding this brown powder to dilute hydrochloric acid and stirring the suspension for several minutes, a black powder was formed. In this process, the amorphous $\text{Cd}(\text{N}_2\text{H}_4)\text{TeO}_3$ was easily

dissolved by HCl and the residual three-dimensional skeleton of CdTe nanocrystallites—highly reactive by virtue of its low crystallinity—reacted spontaneously *in situ* with TeO_3^{2-} to form the nanoporous tellurium architecture. This topotactic reaction can be expressed

as follows:

Because the nanoporous tellurium architecture was formed under ambient conditions, its crystallinity was poor (Fig. 8(a)). The nanoporous architecture was also unstable under irradiation by the electron beam in TEM (see Fig. S-1 in the ESM).

When the hydrazine–cadmium tellurite hybrid microcrystals were annealed at 450 °C for 2 h, the material was converted to a mixture of highly crystalline CdTe and CdTeO₃ (Fig. 5(e)). On treatment of the product with dilute hydrochloric acid, the CdTeO₃ phase dissolved leaving a porous CdTe architecture. The CdTe was relatively unreactive because of its high crystallinity and, unlike the earlier

case, did not react with TeO₃²⁻. Based on the above analysis and results, the complete transformation pathway from hydrazine–cadmium tellurite hybrid microcrystals to porous cadmium telluride and tellurium architectures can be proposed, as illustrated in Scheme 1.

2.5 BET analysis and optical properties of porous cadmium telluride and tellurium architectures

Nitrogen adsorption and desorption isotherms were obtained in order to determine the surface area and porosity of the porous cadmium telluride and tellurium architectures. Figures 10(a) and 10(b) show the nitrogen adsorption–desorption isotherms of the porous cadmium telluride and tellurium, respectively. The BET (Brunauer–Emmett–Teller) surface areas of

Scheme 1 Illustration of transformation pathways from hydrazine–cadmium tellurite hybrid microcrystals to porous tellurium and cadmium telluride architectures

Figure 10 Nitrogen adsorption–desorption isotherms of (a) porous cadmium telluride and (b) nanoporous tellurium. The inserts show the corresponding pore size distributions

cadmium telluride and tellurium are 7.05 m²/g and 14.96 m²/g, respectively, and the BJH (Barrett–Joyner–Halenda) average pore diameters are about 70 nm and 40 nm, respectively. The surface area and pore size of nanoporous tellurium are both better than the corresponding values for porous cadmium telluride, which is consistent with the SEM images. This is the first time that nanoporous semiconducting cadmium telluride and tellurium architectures have been fabricated by thermal decomposition of a hydrazine–cadmium tellurite hybrid material.

The optical properties of the samples were studied by UV–visible spectroscopy, which showed that the band gap of the hydrazine-based hybrid materials was significantly different from those of porous cadmium telluride and tellurium. The absorption edge of the Cd(N₂H₄)TeO₃ hybrid occurs at about 300 nm (Fig. 11(b)), but the absorption edge of the porous CdTe architectures was red-shifted to 850 nm. The UV–visible spectra of both porous CdTe and Te are similar to those of the corresponding bulk materials.

3. Conclusions

A well-defined platelet-like hydrazine–cadmium tellurite hybrid material can be synthesized by a facile reaction under mild conditions in a mixed solvent. The resulting hybrid material was fully characterized by PXRD, elemental analysis, TGA, and XPS; the results were consistent with the formula Cd(N₂H₄)TeO₃.

Figure 11 UV–visible spectra of (a) porous cadmium telluride, (b) Cd(N₂H₄)TeO₃, and (c) nanoporous tellurium

Control over the morphology and evolution of Cd(N₂H₄)TeO₃ with reaction time have been discussed. Because of the high volatility and reducing capacity of hydrazine, Cd(N₂H₄)TeO₃ undergoes a temperature-dependent thermal decomposition. It was found that porous cadmium telluride and nanoporous tellurium architectures can be selectively produced by treating the samples formed by thermal decomposition at different temperatures with hydrochloric acid. BET analysis and a study of the optical properties of the porous samples are also reported. The as-synthesized porous cadmium telluride and tellurium microcrystals have potential uses in sensor devices or as templates for the synthesis of other porous materials.

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