A new generation of alloyed/multimetal chalcogenide nanowires by chemical transformation

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One-dimensional metal chalcogenide nanostructures are important candidates for many technological applications such as photovoltaic and thermoelectric devices. However, the design and synthesis of one-dimensional metal chalcogenide nanostructured materials with controllable components and properties remain a challenge. We report a general chemical transformation process for the synthesis of more than 45 kinds of one-dimensional alloyed/hybrid metal chalcogenide nanostructures inherited from mother template Te$_x$Se$_y$@Se core-shell nanowires with tunable compositions. As many as nine types of monometal chalcogenide alloy nanowires (including AgSeTe, HgSeTe, CuSeTe, BiSeTe, PbSeTe, CdSeTe, SbSeTe, NiSeTe, and CoSeTe) can be synthesized. Alloyed and hybrid nanowires integrated with two or more alloyed metal chalcogenide phases can also be prepared. The compositions of all of these metal chalcogenide nanowires are tunable within a wide range. This protocol provides a new general route for the controllable synthesis of a new generation of one-dimensional metal chalcogenide nanostructures.

INTRODUCTION

Nanostructured metal chalcogenides are highly promising materials for a range of technological applications [including electronic devices (1), photovoltaic devices (2, 3), thermoelectric devices (4, 5), and catalysts (6, 7)] owing to their interesting electrical, optical, and electrochemical properties. One-dimensional (1D) metal chalcogenide nanostructures in particular have been the subject of intensive research because of their unique properties (for example, reduced thermal conductivity) compared to the properties of their corresponding bulk materials (8, 9). Metal chalcogenide hybrids or alloys integrated with two or more chemically distinct metal chalcogenide phases are also extremely attractive because they enhance the functionality of the materials and provide novel properties (10, 11). The demand for the controllable synthesis of 1D metal chalcogenide nanostructures drives us to explore general and convenient synthetic approaches.

A number of synthetic approaches for 1D metal chalcogenide nanostructures have been developed in the past decades, such as chemical vapor deposition (12), organic solution–based high-temperature synthesis (13, 14), oriented-attachment method (15, 16), template-directed method (17, 18), and hydrothermal/solvothermal process (19, 20). Among these methods, chemical transformation (CT), a type of template-directed method, has been one of the most efficient and most popular strategies (21, 22). Recently, uniform Ag$_x$Se nanowires (23, 24) and CdSe nanotubes (25) have been simply synthesized through the CT of selenium (Se) nanowires. A variety of metal telluride nanowires, including Pb$_x$Te (26), Cd$_x$Te (27), Bi$_x$Te$_y$ (28), Ag$_x$Te (29), and La$_x$Te$_y$ (30), have been reported to be converted from tellurium (Te) nanowires. However, the synthesis of 1D metal chalcogenide alloy and hybrid nanostructures by CT has rarely been reported to date. The morphology of the target product is highly dependent on the preexisting template in a CT process. For the synthesis of high-quality 1D metal chalcogenide nanostructures through a CT process, high-quality 1D chalcogen nanostructures are imperatively desired. Although highly uniform Te (31, 32) and Se (33, 34) nanowires have been obtained through various procedures, very few reports on the synthesis of Te/Se alloy (35) or hybrid (36, 37) nanowires can be found in the literature, probably on account of their relatively large differences in chemical properties.

Here we report a straightforward design strategy for the synthesis of Te$_x$Se$_y$@Se core-shell nanowires by epitaxial growth of Se shells on ultrathin Te nanowires. We demonstrate a general and controllable strategy for the synthesis of a brand-new generation of 1D metal chalcogenide alloy and hybrid nanostructures with controllable compositions and multiple functionalities, which are inherited from such Te$_x$Se$_y$@Se core-shell nanowires based on the CT process.

RESULTS

Te$_x$Se$_y$@Se core-shell nanowires

Ultrathin Te nanowires (31) with a diameter of ~7 nm (fig. S1) were selected as substrates for preparing Te$_x$Se$_y$@Se nanowires. Se-dissolved hydrazine hydrate solution was chosen as the Se precursor. Te$_x$Se$_y$@Se nanowires were prepared by slowly adding the Se precursor to the Te nanowire aqueous solution and by aging it at 80°C for 12 hours. By tuning the amount of the Se precursor added, we were able to prepare Te$_x$Se$_y$@Se core-shell nanowires with different Te/Se ratios and diameters. A transmission electron microscopy (TEM) image of as-produced core-shell nanowires with a Te/Se precursor ratio of 1:4 is shown in Fig. 1A, demonstrating the perfect wire morphology and a relatively uniform size distribution with an average diameter of 18.7 ± 1.5 nm. This diameter is much larger than that of Te nanowires (~7 nm), indicating that a Se shell is grown onto the Te nanowire. X-ray diffraction (XRD) pattern (Fig. 1B) shows characteristic peaks for trigonal Te (t-Te) and trigonal Se (t-Se) corresponding to the core and shell, respectively. No peaks for impurities such as TeO$_2$ or SeO$_2$ can be observed. The peaks indexed to t-Te show an obvious shift to larger degrees compared to Te nanowires, which may have resulted from the formation of a Te$_x$Se$_y$ alloy core originating from the insertion of an Se atom into the Te core (38). X-ray photoelectron spectra (fig. S2) indicate that there are only
elemental Se and Te in the core-shell nanowires. Further character-
ization of the nanowires was performed using high-resolution TEM
(HRTEM). The image presented in Fig. 1C highlights a section of a
single nanowire, which reveals a clear interface between the core
and the shell. Lattice spacings of 3.0 and 3.2 Å are indexed to the (101)
plane of t-Se and the (101) plane of Te$_x$Se$_{1-x}$ alloy, respectively. The amor-
phous shell observed in HRTEM is caused by the instability of Se upon
exposure to a high-energy electron beam (fig. S3). High-angle annular
dark field (HAADF) scanning TEM (STEM) energy-dispersive x-ray
spectroscopy (EDS) line scanning analysis (Fig. 1D) also reveals com-
positional variation in a single nanowire, suggesting that Te is mostly
present in the center and that more Se is distributed in the shell. This
is an additional piece of evidence confirming the core-shell structure.
Because of spurious signals in EDS coming from the surrounding areas,
line scan profiles do not correspond to the core-shell positions (charac-
terized by a very small scale and instability of Se upon exposure to an
electron beam). Images in Fig. 1 (E and F) show elemental mapping of a
single Te$_x$Se$_{1-x}$@Se nanowire with a core-shell structure.

Nanowires with a much higher Te/Se ratio (4:1) were prepared to
further understand the formation of the Te$_x$Se$_{1-x}$ core. As illustrated in
fig. S4A, no core-shell nanowires can be observed in TEM analysis. Diffraction data (fig. S4B) suggest that the diffraction peaks of these
nanowires are shifted to larger degrees compared to the diffraction
peaks of Te nanowires, ruling out the possibility of phase separation
and thus preliminarily confirming the formation of Te$_x$Se$_{1-x}$ alloy. Fur-
ther evidences for the formation of Te$_x$Se$_{1-x}$ alloy are supplied by HRTEM
and elemental mapping analyses (fig. S4, C to E). Considering the fact
that the radius of the Se atom is smaller than that of Te, Se atoms can
be inserted into Te nanowires to form a Te$_x$Se$_{1-x}$ alloy. On the basis of
the phase diagram of Se–Te (39), Se and Te are completely miscible in
each other in the liquid and solid states. However, we obtained core-
shell nanowires instead of alloy nanowires when the Te/Se ratio was
set to 1:4. We attributed this to the relatively low aging temperature. In
fact, we obtained TeSe$_4$ alloy nanorods when the aging temperature
was increased to 120°C (fig. S5). Therefore, we speculate that the Te nano-
wire skeleton is rigid at an aging temperature of 80°C and that this
causes a solubility limit of Se in the Te nanowire skeleton. Thus, we
suggest a possible mechanism for the formation of Te$_x$Se$_{1-x}$@Se core-shell
nanowires. Se atoms are initially released from the Se precursor and
inserted into Te nanowires after the addition of the Se precursor. After the
Te nanowire skeleton is saturated with Se atoms, the rest of the Se atoms
are epitaxially deposited onto the skeleton and, finally, the Te$_x$Se$_{1-x}$@Se
core-shell nanowires are formed.

A series of Te$_x$Se$_{1-x}$@Se core-shell nanowires were prepared by
varying the Te/Se precursor ratio. As the Te/Se precursor ratio changes,
no obvious difference in morphology and crystallographic structure
can be observed. TEM observations (fig. S6) indicate that the diameters
of Te$_x$Se$_{1-x}$@Se nanowires become larger with increasing amounts of
the Se precursor. XRD studies (fig. S7) indicate that the peaks corre-
sponding to the Te$_x$Se$_{1-x}$ cores of all of the samples are at the same
diffraction angle, implying that the Te$_x$Se$_{1-x}$ cores of all of the samples
have the same component. This is an additional indirect evidence con-
firming that the Te nanowire skeleton can be saturated by Se atoms.
The intensities of the peaks indexed to the Se shell increase with in-
creasing amounts of the Se precursor, demonstrating that the Se contents
of Te$_x$Se$_{1-x}$@Se nanowires follow the same variation trend.
of Te$_x$Se$_y$@Se nanowires prepared with different Te/Se precursor ratios were measured using EDS analysis (fig. S8), which directly identifies the previously discussed variation trend. We emphasize that Te$_x$Se$_y$@Se nanowires can be easily scaled up because of the simple preparation and scaled-up synthesis of the Te nanowire template (40). The morphology and uniformity of Te$_x$Se$_y$@Se nanowires remain the same even when the synthesis is scaled up 12 times (fig. S6B).

**Monometal chalcogenide alloy nanowires**

Only elemental Se, Te, hydrazine, residual poly(vinyl pyrrolidone) (PVP), and water were found in the obtained Te$_x$Se$_y$@Se nanowire solution, without any other impurities. Thus, we can directly perform the CT process in the Te$_x$Se$_y$@Se nanowire solution simply by adding the corresponding metal precursors and extra hydrazine, if necessary. Through the CT of Te$_x$Se$_y$@Se nanowires, we obtained nine types of monometal chalcogenide (MSeTe) alloy nanowires, including AgSeTe, HgSeTe, CuSeTe, BiSeTe, PbSeTe, CdSeTe, SbSeTe, NiSeTe, and CoSeTe (fig. S9). A typical TEM image of AgSeTe nanowires (Fig. 2A) obtained by the CT of Te$_x$Se$_y$@Se nanowires ([Te]:[Se] = 1:4) demonstrates that they are uniformly wire-like shaped. HRTEM analysis (fig. S10A) indicates the single-phase nature of as-synthesized AgSeTe nanowires. Obviously, all of the peaks can be indexed as orthorhombic Ag$_2$Se [powder diffraction file (PDF) no. 24-1041] with a slight shift to smaller degrees, preliminarily certifying the formation of AgSeTe alloy. An HRTEM image of a single AgSeTe nanowire (Fig. 2B) shows clear lattice fringes without any grain boundaries, further implying the single-phase nature of the nanowire. A selected area electron diffraction (SAED) pattern is also provided (Fig. 2B, inset) to further confirm the single-phase nature of AgSeTe nanowires. Images in Fig. 2C show elemental mapping results for Ag (magenta), Se (yellow), and Te (green), indicating a relatively even distribution of Se. In a single AgSeTe nanowire, Te is distributed along the whole nanowire, though not very uniformly. This is an additional direct piece of evidence for the ternary alloy structure of AgSeTe nanowires.

Figure 2 (D to H) shows TEM images of eight types of MSeTe alloy nanowires. The alloy structure and composition of the obtained MSeTe nanowires are confirmed using XRD, HRTEM, and EDS (figs. S10 to S12) analyses.

Using the solution of Te$_x$Se$_y$@Se core-shell nanowires with different Te/Se ratios, we can successfully synthesize MSeTe alloy nanowires with different Te/Se ratios, taking CdSeTe and BiSeTe as examples (fig. S13). With increasing Se content in the Te$_x$Se$_y$@Se nanowire solution, the diameters of the nanowires obviously get larger and the peaks of XRD patterns shift to larger degrees, indicating the unchanged crystallographic structure and increasing Se content of MSeTe nanowires. Inductively coupled plasma (ICP) atomic emission spectrometry (AES) measurements (table S1) are performed to certify this variation trend.

To date, there are two main mechanisms for the transformation of chalcogen nanostructures into metal chalcogenide nanostructures in aqueous solution. One mechanism involves the disproportionation of chalcogen, which is strongly dependent on the alkalinity of the solution (19). The other mechanism touches on the reduction of metal ions to metal atoms and the reaction between elemental metal and elemental chalcogen, which critically rely on the reduction potential of metallic species and the reducing capacity of reducing agents (27). The pH value

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**Fig. 2. Characterization of MSeTe nanowires.** (A) TEM image of AgSeTe nanowires. (B) HRTEM image of AgSeTe nanowires. Inset: A SAED pattern. (C) Elemental maps of Ag (magenta), Se (yellow), and Te (green). (D to K) TEM images of the remaining eight types of MSeTe nanowires: (D) HgSeTe, (E) CuSeTe, (F) BiSeTe, (G) PbSeTe, (H) CdSeTe, (I) SbSeTe, (J) NiSeTe, and (K) CoSeTe.
of freshly prepared Te\textsubscript{0.8277}Se\textsubscript{0.1723}@Se core-shell nanowires is about 10.2. This weak alkaline condition is unlikely to initiate the disproportionation of elemental chalcogen (41). During the CT of Te\textsubscript{0.8277}Se\textsubscript{0.1723}@Se core-shell nanowires, only hydrazine hydrate was used as alkaline source. However, the dissociation constant of hydrazine is about 7.9 \times 10^{-6} (pK\textsubscript{a} = 8.1), which is unlikely to supply a strong alkaline condition even with a relatively high concentration. Thus, the first mechanism is not possible, whereas the second mechanism is reasonable for the evolution of MSeTe. Cellular reaction spontaneously occurs only when the cell potential is higher than zero. For metallic species with a reduction potential lower than −0.8277 V, reduction of the corresponding metal ion to metal atom in alkaline solution is impossible because water will be reduced first until all of the reducing agents had been exhausted, whereas the critical value for the reduction of metal ion in acidic solution is zero. Nine kinds of MSeTe (M = Ag, Hg, Cu, Bi, Pb, Cd, Sb, Ni, Co) can be theoretically synthesized in the Te\textsubscript{x}Se\textsubscript{1−x}@Se solution according to the standard reduction potential (table S2), consistent with our experiment results. Some other MSeTe nanowires can also be theoretically obtained from the Te\textsubscript{x}Se\textsubscript{1−x}@Se solution for the same reason (for example, TiSeTe nanowires). We also tried to prepare MSeTe, whose metallic species has a reduction potential lower than −0.8277, but this attempt failed. For example, the product we obtained from FeSeTe (fig. S14, A and B) was not FeSeTe alloy nanowire but a mixture of elemental Se, Te, and some amorphous matters, even though as much as 20 ml of hydrazine was used as a reducing agent. This result also provides an additional proof for the negation of the first mechanism. Because the reducing capacity of hydrazine is dependent on its concentration, we need to tune the concentration of hydrazine according to the reactivity of metallic species. During the evolution of AgSeTe, the product obtained was a mixture of elemental silver and AgSeTe when only AgNO\textsubscript{3} was added to the Te\textsubscript{x}Se\textsubscript{1−x}@Se solution (fig. S14, C and D). We conjecture that the concentration of hydrazine in the Te\textsubscript{x}Se\textsubscript{1−x}@Se solution is too high for the reduction of Ag\textsuperscript{+}, which leads to the excessively fast generation, nucleation, and growth of Ag atoms and thus impedes the reaction between Ag atoms and chalcogen atoms. Hence, NH\textsubscript{4}SCN is added into the AgNO\textsubscript{3} solution to form AgSCN colloids and thus slows the generation of silver atoms on the basis of the much lower reduction potential of AgSCN/Ag compared to Ag\textsuperscript{+}/Ag. As a result, we can successfully synthesize pure-phase AgSeTe nanowires. For the synthesis of HgSeTe, CuSeTe, PbSeTe, BiSeTe, SbSeTe, and CdSeTe, the concentration of hydrazine in Te\textsubscript{x}Se\textsubscript{1−x}@Se solution is suitable. However, for CoSeTe and NiSeTe, additional hydrazine is required for the very low potentials of Co(OH)\textsubscript{2}/Co and Ni(OH)\textsubscript{2}/Ni. Under a low concentration of hydrazine, the product obtained was a mixture of MSeTe and M(OH)\textsubscript{2} (M = Co, Ni) (fig. S15). However, as soon as the concentration of hydrazine reached the critical level, pure-phase CoSeTe and NiSeTe were obtained.

Multimetal chalcogenide alloy and hybrid nanowires

Multimetal chalcogenide (MMC) alloys and hybrid nanowires were simply prepared by adding two or more types of metal precursor in the same batch. On the basis of the successful synthesis of nine kinds of MSeTe, as many as 36 kinds of bimetal chalcogenide (BMC) alloys or hybrids are expected to be acquired. Actually, all of them were successfully prepared (Fig. 3 and Table 1). As shown in Fig. 3, all of the BMC samples obtained were nanowires. In detail, we obtained three kinds of nanowires, namely, M\textsubscript{1}M\textsubscript{2}SeTe alloy nanowire (M\textsubscript{1}M\textsubscript{2}), M\textsubscript{1}SeTe/M\textsubscript{2}SeTe hybrid nanowire (M\textsubscript{1}/M\textsubscript{2}), and M\textsubscript{1}SeTe@M\textsubscript{2}Se core-shell nanowire (M\textsubscript{1}@M\textsubscript{2}). When the Ag and Cu precursors were added in the same batch, we obtained AgCuSeTe alloy nanowires instead of Ag/Cu hybrid or a mixture of AgSeTe and CuSeTe. TEM analysis of AgCuSeTe is shown in Fig. 3 (1). The XRD pattern of the product (fig. S16A) can be nearly indexed as orthorhombic CuAgSe (PDF no. 25-1180). The appearance of a new phase indicates the alloy nature of the product. The HRTEM image of a typical AgCuSeTe nanowire (Fig. 4A) demonstrates clear lattice fringes without obvious grain boundaries, further confirming its alloy nature. Lattice spacings of 4.13 and 6.34 Å can be indexed to the (100) and (001) planes of AgCuSeTe alloy, respectively. A SAED pattern (Fig. 4A, inset) also illustrates the formation of alloy. An additional piece of evidence that confirms the alloy structure is supplied by EDS elemental mapping (Fig. 4C), which indicates the almost homogeneous distribution of the four elements. Unlike the situation of AgCuSeTe alloy, Cu/Pb metal chalcogenide hybrid nanowires [Fig. 3 (17)] were obtained when Cu and Pb precursors were added in the same batch. XRD
(fig. S16C) and HRTEM (Fig. 4B) analyses were carried out to confirm the hybrid structure. Obviously, there are two sets of diffraction peaks in the XRD pattern, indicating that there are two phases in the product. The two sets of peaks can be indexed to CuSeTe and PbSeTe, respectively. A clear grain boundary in a single Cu/Pb hybrid nanowire was observed on HRTEM analysis, directly confirming its hybrid nature. A lattice spacing of 3.33 Å can be indexed to the (111) plane of CuSeTe, whereas lattice spacings of 3.06 and 3.54 Å can be indexed to the (200) and (111) planes of PbSeTe, respectively. A SAED pattern of Cu/Pb nanowires (Fig. 4B, inset) also indicates the binary phases of Cu/Pb nanowires. Further verification is provided by EDS elemental mapping analysis (Fig. 4D). In a single nanowire, Se and Te atoms uniformly distribute whereas Cu and Pb atoms randomly distribute on the nanowire. When Cd and Ni precursors were mixed in one synthetic system, we obtained Ni@Cd core-shell nanowires [Fig. 3 (32)]. The two-phase structure is confirmed by XRD (fig. S16E). The core-shell structure is simply verified on EDS elemental mapping analysis (Fig. 4E), in which Se is uniformly distributed in the whole nanowire and Cd prefers to reside in the shell, whereas Ni and Te only appear in the core. The structures of other BMC alloys and hybrids are preliminarily analyzed by XRD (figs. S17 to S20) and TEM observations (Fig. 3) and thus need further structural analyses.

When more than two kinds of metal precursors were synthesized, we also realized the growth of the corresponding metal chalcogenides onto the same nanowire. Cu/Hg/Pb and Cu/Hg/Pb/Bi MMC hybrids (fig. S21) were produced. Through TEM observations (fig. S21, A and D), we found that there were only pure nanowires without any other morphologies in the product. XRD studies (fig. S21, C and F) suggested that there were no impurities in the product. EDS elemental mapping analyses (fig. S21, B and E) were performed to negate the possibility of the formation of a mixture of different MSeTe alloy nanowires. The results revealed that all of the involved metal elements almost homogeneously distributed in a single nanowire. On the basis of the abovementioned results, we can obtain any alloy or hybrid nanowires formed by an arbitrary combination of the nine kinds of MSeTe. Just like the synthesis of MSeTe, the Te/Se ratios and the contents of the metal elements in MMC alloys and hybrids can also be tuned simply by adjusting their ratios in the precursors. We have successfully achieved the rough composition regulation of Cu/Pb hybrid nanowires and BiPbSeTe alloy nanowires (fig. S22).

**Formation mechanism of metal chalcogenide alloy and hybrid nanowires**

The possible mechanism for the formation of metal chalcogenide alloy and hybrid nanowires is illustrated in Fig. 5, in which the formation of MSeTe (Fig. 5A) and BMC (Fig. 5B) has been chosen to exhibit the mechanism. Considering the core-shell nature of Te$_x$Se$_y$@Se nanowires and the higher chemical reactivity of Se to metal atoms compared to Te, MSeTe@MSe core-shell nanowires are expected to form when one type of metal precursor is added to the Te$_x$Se$_y$@Se nanowire solution. However, actual MSeTe alloy nanowires are obtained. We ascribe the experimental results to the precipitation of metal hydroxides or other insoluble substances (MX) originating from the alkalinity of the Te$_x$Se$_y$@Se nanowire solution or the extra precipitants added. The formation of insoluble MX impedes the homogeneous reaction between the Te$_x$Se$_y$@Se nanowire and the metal precursor, but it will facilitate CT in many grains of limited sizes along the nanowire. Thus, many MSeTe alloy fragments are formed along the Te$_x$Se$_y$@Se nanowire through a mutual diffusion process (17), during which the outward diffusion of Te atoms and the inward diffusion of metal atoms take place at the same time. Finally, MSeTe alloy nanowires are formed after the completion of CT. If the net diffusion of atoms is outward, MSeTe nanotubes with rough surfaces (BiSeTe, PbSeTe, and CoSeTe) will finally form through the nanoscale Kirkendall effect (28, 42). Otherwise, solid nanowires will be formed. As an example, the transformation of PbSeTe (fig. S23) is presented to illustrate this mechanism. Obviously, PbO$_x$ is formed in

**Fig. 4. Characterization of AgCuSeTe, Cu/Pb, and Ni@Cd nanowires.** (A and B) HRTEM images and SAED patterns (insets) of AgCuSeTe and Cu/Pb. (C to E) Elemental maps of AgCuSeTe, Cu/Pb, and Ni@Cd.
the early stages of the CT process (fig. S23, A and D), corresponding to
the insoluble matters of metal precursors. This is exactly the reason
for the formation of nanowires with many fragments (fig. S23A, inset),
as described above. With the prolonged reaction time, PbSeTe nano-
tubes are finally formed, and all of PbOx disappears.

The morphologic evolution of BMC nanowires is affected by the
same factors affecting MSeTe nanowires. Here, we describe the struc-
tural evolution of BMC nanowires. Because the reduction potentials
of the different metallic species differ from one another, there is, theoreti-
cally, a reduction sequence if two or more kinds of metal ions are
involved in one synthesis without regard to kinetics. According to
the standard reduction potential (in alkaline solution), we have ob-
tained a reduction sequence as follows: Ag (reduced first), Hg, Cu,
Bi, Pb, Cd, Sb, Ni, and Co. Thus, metal precursor M1 will be reduced
first if metal precursors M1 and M2 are added together, assuming that
M1 has a more positive reduction potential. Two possible reactions can
take place. The main reaction is the formation of many M1SeTe frag-
ments on TexSy@Se nanowires through the reaction between the
TeXSy@Se nanowire and the preformed M1X (Fig. 5B, reaction 1).
In this case, M2SeTe fragments are formed on the unreacted part of
the TexSy@Se nanowire and, finally, the M1/M2 hybrid is formed. If
the lattice mismatch between M1SeTe and M2SeTe fragments is small
enough, M1M2SeTe alloy is favored to form after a certain period of
ripening. A lattice mismatch larger than ~4% can induce islands or misfit
dislocations, except for the growth of a few atomic layers (43). The lat-
tice mismatch between the (111) plane of Ag2Se (PDF no. 24-1041) and
the (111) plane of Cu2−xSe (PDF no. 06-0680) is as small as 0.09%; thus,
AgCuSeTe alloy nanowires are formed when Ag and Cu precursors are
added together. However, if the lattice mismatch is too large, the final
product will be a hybrid structure. Cu/Pb hybrid nanowires are formed
when Cu and Pb precursors are added together because the lattice mis-
match between the (111) plane of Cu2−xSe and the (111) plane of PbSe
(PDF no. 06-0354) reaches up to 5.8%. The other reaction is the forma-
tion of a CdSe shell composed of CdSe nanoparticles on the TexSy@Se
nanowire, which occurs when the Cd precursor and other metal precu-
sors (Sb, Ni, and Co) with reduction potentials more negative than that of
the Cd precursor are added together in the same batch (Fig. 5B, re-
action 2). This could be caused by the very small size of the preformed
Cd(OH)2. In this case, MSeTe@CdSe (Sb, Ni, and Co) core-shell nano-
wires are obtained.

**DISCUSSION**

In summary, we report a controllable template-directed CT route for
the synthesis of a new generation of 1D alloyed/MMC nanowires. Highly
reactive TexSy@Se core-shell nanowires with tunable Te/Se ratios are
first prepared to serve as templates. Nine kinds of MSeTe alloy nano-
wires [that is, MSeTe (M = Ag, Hg, Cu, Bi, Pb, Cd, Sb, Ni, Co)] can be
prepared using a simple CT process. Furthermore, MMC alloys or
hybrids integrated with two or more types of MSeTe have also been
prepared through an identical procedure, except that two or more types
of metal precursors have been added together. The compositions
of MSeTe and MMC nanowires are believed to be controllable in a wide
range. Thus, this approach represents a new general route for the syn-
thesis of a new generation of 1D metal chalcogenide nanostructures
with controllable compositions and multiple functionalities, which are
expected to find broad applications in many fields.

**MATERIALS AND METHODS**

**Materials**

PVP (K30), hydrazine hydrate (85%, w/w), acetone, aqueous ammonia
solution (25 to 28%, w/w), Se powder (99%), NH4SCN, AgNO3, HgCl2,
copper acetate monohydrate [Cu(Ac)2·H2O], Pb(NO3)2, Cd(NO3)2·4H2O,
Co(NO3)2·6H2O, Ni(NO3)2·6H2O, Bi(NO3)3·5H2O, and potassium ant-
imony tartrate hemihydrate (K2SbC4H4O7·½H2O) were purchased.
A hydrothermal process was used to carry out the CT of Te parameters are shown in Table S3. at room temperature for about 30 min. The autoclave was sealed and Teflon-lined stainless steel autoclave under vigorous magnetic stirring. Finally, the mixed solution was kept at 80°C for another 12 hours without stirring.

Synthesis of Te₆Se₆@Se core-shell nanowires
First, ultrathin Te nanowires were prepared using our previously developed method (31). Te₆Se₆@Se core-shell nanowires with different Te/Se molar ratios can simply be synthesized by tuning the molar ratios between Te nanowires and Se powder. In a typical synthesis (for example, [Te]:[Se] = 1:4), 37 ml of freshly prepared Te nanowires (~0.4 mmol) was precipitated by adding about 100 ml of acetone. The precipitated Te nanowires were dispersed in 79 ml of DIW with magnetic stirring at room temperature for about 1 hour. Se powder (1.6 mmol) dissolved in 1 ml of hydrazine hydrate (85%, wt/wt %) was slowly added to the previous solution. The mixed solution was kept at 40°C for 12 hours with magnetic stirring. Finally, the mixed solution was kept at 80°C for another 12 hours without stirring.

Synthesis of MSeTe nanowires
In a typical synthesis of Ag₂SeTe nanowires, 0.9 mmol of AgNO₃, 20 ml of DIW, and 5 ml of NH₄SCN solution (1 M) were first mixed in a 100-ml conical flask to form a white suspension under mild magnetic stirring at room temperature. Twenty milliliters of Te₆Se₆@Se solution ([Te]:[Se] = 1:4; about 0.5 mmol of Se and Te in total) was added to the previous solution and finally reacted in a 80°C water bath for 8 hours. A similar procedure was used to prepare HgSeTe and CuSeTe nanowires, except for the nonuse of NH₄SCN. A hydrothermal process was used to prepare the remaining six types of MSeTe nanowires. Certain amounts of metal precursor, DIW, and hydrazine hydrate (85%, wt/wt %), and 40 ml of Te₆Se₆@Se solution ([Te]:[Se] = 1:4) were mixed in a 100-ml Teflon-lined stainless steel autoclave under vigorous magnetic stirring at room temperature for about 30 min. The autoclave was sealed and maintained at a certain temperature for 12 hours. Detailed reaction parameters are shown in Table S3.

Synthesis of BMC nanowires
A hydrothermal process was used to carry out the CT of Te₆Se₆@Se into BMC alloy and hybrid nanowires. Certain amounts of M₃ and M₂ precursors (M₁,M₂ = Ag, Hg, Cu, Pb, Cd, Co, Ni, Bi, Sb) and DIW were mixed in a 100-ml Teflon-lined stainless steel autoclave to form a homogeneous solution. Forty milliliters of Te₆Se₆@Se solution ([Te]:[Se] = 1:4) and a certain amount of hydrazine hydrate were added to the former solution with vigorous magnetic stirring at room temperature for about 30 min. Finally, the autoclave was closed and maintained at a certain temperature for 12 hours. Particularly, 5 ml of NH₄SCN solution (1 M) was demanded to be added first to prepare the Ag-based BMC nanowires. Detailed reaction conditions are listed in Table S4.

Synthesis of MMC nanowires
We chose Cu/Hg/Pb and Cu/Hg/Pb/Bi hybrid nanowires as examples to demonstrate the synthesis of MMC nanowires through the CT of Te₆Se₆@Se nanowires. In a typical synthesis of Cu/Pb/Hg hybrid nanowires, 0.9 mmol of Cu(OAc)₂·H₂O, 0.45 mmol of HgCl₂, 0.45 mmol of Pb(NO₃)₂, and 15 ml of DIW were mixed in a 100-ml Teflon-lined stainless steel autoclave, and 60 ml of Te₆Se₆@Se solution ([Te]:[Se] = 1:4) was poured into the autoclave with strong magnetic stirring for about 30 min. Five milliliters of hydrazine was put into the above solution. Finally, the autoclave was maintained at 160°C for 12 hours. The synthesis of Cu/Pb/Hg/Bi hybrid nanowires followed an identical procedure, except that the metal precursors were replaced by 0.72 mmol of Cu(OAc)₂·H₂O, 0.36 mmol of HgCl₂, 0.36 mmol of Pb(NO₃)₂, and 0.24 mmol of Bi(NO₃)₃·5H₂O.

Instrumentation
XRD analyses were carried with a Japan Rigaku DMax-γA rotation anode x-ray diffractometer equipped with graphite monochromatized Cu-K radiation (λ = 1.54178 Å). TEM images were obtained with a Hitachi H-7650 microscope at 100 kV. HRTEM observations were performed using a JEOL ARM-200F or JEOL-2010F transmission electron microscope with an acceleration voltage of 200 kV. SAED and STEM EDX element mappings and line scans were carried out with a JEOL ARM-200F transmission electron microscope. EDS analyses were obtained using a JEOL-2010F transmission electron microscope equipped with the Oxford INCA EDS system. X-ray photoelectron spectroscopy (XPS) studies were carried out using an ESCALAB-MKII x-ray photoelectron spectrometer with Mg Kα radiation as exciting source. ICP-AES measurements were conducted using an Atomscam Advantage Spectrometer (Thermo Ash Jarrell Corporation).

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/1/10/e1500714/DC1
Fig. S1. TEM image of Te nanowires.
Fig. S2. XPS spectra of Te₆Se₆@Se nanowires ([Te]:[Se] = 1:4).
Fig. S3. Morphologic changes in Te₆Se₆@Se core-shell nanowires ([Te]:[Se] = 1:4) upon exposure to an electron beam.
Fig. S4. Characterization of Te₆Se₆ alloy nanowires ([Te]:[Se] = 4:1).
Fig. S5. Characterization of as-synthesized Te₆Se₆ alloy nanorods.
Fig. S6. TEM images of Te₆Se₆@Se nanowires with different Te/Se precursor ratios.
Fig. S7. XRD patterns of Te₆Se₆@Se nanowires with different Te/Se precursor ratios.
Fig. S8. EDS spectra of Te₆Se₆@Se nanowires with different Te/Se precursor ratios.
Fig. S9. Photographs of as-prepared MSeTe nanowires.
Fig. S10. XRD patterns of MSeTe nanowires.
Fig. S11. EDS spectra of MSeTe nanowires.
Fig. S12. HRTEM images and corresponding fast Fourier transform patterns of MSeTe nanowires.
Fig. S13. TEM images and XRD patterns of CdSeTe and BiSeTe nanowires synthesized by the CT of Te₆Se₆@Se nanowires with different Te/Se ratios.
Fig. S14. TEM images and XRD patterns of samples FeSeTe and AgSeTe (prepared without NH₄SCN).
Fig. S15. TEM images and XRD patterns of CuSeTe and NiSeTe nanowires ([Te]:[Se] = 1:4) prepared with different amounts of hydrazine.
Fig. S16. XRD patterns and EDS spectra of obtained AgCuSeTe, Cu/Pb, and NiCd Cd nanowires.
Fig. S17. XRD patterns of obtained BMC alloy nanowires (I).
Fig. S18. XRD patterns of obtained BMC hybrid nanowires (II).
Fig. S19. XRD patterns of obtained BMC hybrid nanowires (III).
Fig. S20. XRD patterns of obtained BMC hybrid nanowires (IV).
Fig. S21. TEM images, elemental maps, and XRD patterns of the two types of MMC hybrid nanowires obtained.
Fig. S22. TEM images and XRD patterns of Cu/Pb and Bi/Pb nanowires prepared through the CT of Te₆Se₆@Se nanowires ([Te]:[Se] = 1:4).
Fig. S23. Characterization of PbSeTe samples obtained from different synthesis stages.
Table S1. Composition of CdSeTe and BiSeTe nanowires synthesized by the CT of Te₆Se₆@Se nanowires with different Te/Se ratios.
Table S2. Standard reduction potentials excerpted from the CRC Handbook of Chemistry and Physics, 90th Edition (CRC Press, 2010).
Table S3. Detailed reaction parameters for the synthesis of MSeTe (Pb, Cd, Co, Ni, Bi, and Sb) nanowires.
Table S4. Detailed reaction conditions for the synthesis of BMC nanowires.
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