Solution phase synthesis of large-area ultra-thin two dimensional layered Bi$_2$Se$_3$: role of Cu-intercalation and substitution

Bapi Pradhan$^1$, Amit Dalui$^{1,2,3}$, Susmita Paul$^1$, Dipanwita Roy$^1$ and Somobrata Acharya$^{1,3}$

$^1$ School of Applied and Interdisciplinary Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India
$^2$ Department of Chemistry, Jogamaya Devi College, Kolkata 700026, India
$^3$ Authors to whom any correspondence should be addressed.
E-mail: amitdalui@gmail.com and camsa2@iacs.res.in

Keywords: layered materials, Cu$^0$ intercalation, electronic properties, CuI substitution, two-dimensional Bi$_2$Se$_3$ nanosheets

Abstract

Intercalation of high densities of guest species without affecting the host lattice is challenging. Here we report on a general solution-based synthesis route to intercalate high densities of zero-valent copper into layered Bi$_2$Se$_3$ nanosheets at room temperature. We develop a solution phase synthesis route to design large area single-crystalline two-dimensional ultrathin Bi$_2$Se$_3$ nanosheets with micron dimensions. Layered Bi$_2$Se$_3$ nanosheets possess rhombohedral crystal structure where the Bi and Se hexagonal planes remain in close stacked configuration forming quintuple layers along the c-direction. The coupling between two quintuple layers is predominantly van der Waals type, which allows intercalating smaller guest zero-valent copper within the layers of Bi$_2$Se$_3$ nanosheets. Such intercalation of guest species without affecting the lattices of Bi$_2$Se$_3$ is challenging considering the change in oxidation state of copper, which limits the intercalant concentration. Additionally, we show that the use of Cu$^1$-amine complex at high temperature reaction conditions yields CuI substituted Cu$^1$-Bi$_2$Se$_3$ nanosheets disrupting the host lattice of Bi$_2$Se$_3$ nanosheets. We have explored the role of intercalation and substitution on the electronic properties of pristine Bi$_2$Se$_3$ nanosheets. Development of new synthetic strategy for the synthesis of ultra-thin larger area 2D layered Bi$_2$Se$_3$ nanosheets and understanding the role of metal intercalation and substitution hold promises for fundamental understanding and energy related applications.

1. Introduction

Recently, semiconductor metal chalcogenide nanocrystals (NCs) remain in the centre of interest owing to the large arena covered ranging from fundamental research to technological applications [1–13]. Highly emissive cadmium chalcogenide NCs are used for light emitting diode applications [2, 4, 14]. Whereas lead chalcogenide NCs shows potential towards photovoltaic applications [3, 4]. Zinc and copper based chalcogenide NCs shows good catalytic properties for photocatalytic oxygen reduction and hydrogen evolution [5, 15–18]. Various alloyed metal chalcogenide NCs are used in thermoelectric applications [19]. Layered metal chalcogenide NCs are vastly investigated in the field of supercapacitor, Li-ion battery, sensor and memory devices application [20, 21].

Despite of the intense research on the synthesis and application of metal chalcogenides NCs, more extensive research is prerequisite in order to gain control over size, shape, crystallographic phase, in addition to the underlying formation mechanism of NCs [22]. Recently, two-dimensional (2D) metal chalcogenide NCs showed a variety of surface active applications including electrochemical and topological insulators [23–39]. In 2D NCs, the charge carriers are confined along the thickness, however, are allowed to move along the lateral plane. Owing to the active basal planes and edges, 2D nanosheets can be modified by chemical functionalization by doping or intercalation to incorporate additional reactive sites. 2D nanosheets possess the ability to intercalate ions in between the adjacent layers and can provide intercalation pseudocapacitance [23–25].
rigid porous 3D materials, the nature of 2D nanosheets favours fast ionic transport through 2D channels. Due to their sub-nanometer thickness, 2D nanosheet have a high packing density that leads to a high volumetric capacitance, which is significant for manufacturing thin-film supercapacitors and microsupercapacitors [23]. Tuning the amount of intercalant concentration yields many surprising and unusual physical and chemical phenomena [24–27]. Although intercalation of alkali metals such as lithium can be high because of the small size, however, intercalation concentrations are mostly limited by the ionic nature of the intercalant [24]. The predominantly ionic nature of a guest species requires either a change in the host lattice oxidation states or the presence of vacancies to maintain charge neutrality, thus limiting the intercalant concentration. Intercalation of ionic guest species often initiates cation exchange reaction with host cation by substitution, which results in alloyed nanocrystals with different physical and chemical properties compared to the host NCs [7]. Additionally, formation of alloy may lead to the strain within the NCs due to size mismatch between the guest and host cations [7]. In contrary, zero-valent intercalants do not change the oxidation state of the host lattice, thus allowing the possibility of high concentration of intercalation [28–32]. Zero-valent intercalants manifest unusual physical effects such as superlattice structures and incommensurate charge density waves [30, 33–37]. The topological insulator characteristics of bismuth chalcogenides is well established from the recent theoretical and experimental studies [36–39]. The surface topological property is related to the shape of the bismuth chalcogenide NCs [37, 38, 40].

Depending on the choice of the cation precursor and reaction conditions, it is feasible to obtain either intercalated or substituted alloyed NCs. Recently, a technique has been developed using dilute concentration of metal in solution phase to intercalate high densities of zero-valent metals into layered materials [30]. For layered Bi2Se3 crystal, it is possible to intercalate zero-valent Cu+ in the van der Waals gap to obtain copper intercalated Bi2Se3 NCs without disturbing the host lattice framework. On the other hand, foreign cation Cu+ can undergoes cation exchange reaction which allows the substitution of the original host cation framework resulting in alloyed Bi2Se3 NCs [41, 42]. Notably, replacement of BiIII with Cu+ will cause strain in the host crystal lattice considering the difference in the effective ionic radii of BiIII (1.03 Å) and Cu+ (0.77 Å) in addition to the overall charge imbalance in the crystal. Additionally, the insertion of Cu+ beyond in an excess limit may cause Cu2-,Se NCs formation by complete cation exchange reaction [34, 35].

Hence, the development of new synthetic strategy for the synthesis of 2D shape-controlled Bi2Se3 nanosheets and understanding the role of metal intercalation or substitution are important for fundamental interest and technological applications. Here we demonstrate a rapid synthetic route for designing large area ultrathin single-crystalline Bi2Se3 nanosheets. The growth mechanism of Bi2Se3 nanosheets involves oriented attachment mechanism where small Bi2Se3 NCs undergo oriented attachment followed by epitaxial recrystallization. The layered Bi2Se3 nanosheets consist of typical thickness of two quintuple layers (QLs) with a van der Waals gap within the layers. We observed that the overall shape of the nanosheets is sensitive to the synthesis temperature, nature of surfactants and annealing time. Short chain amine and acid surfactants and relatively low reaction temperature greatly enlarged the lateral dimension of the nanosheets. Furthermore, we are able to intercalate 30% of Cu+ within the layers of Bi2Se3 nanosheets without affecting the host lattice. On the other hand, use of Cu+ salt substitutes bismuth from the host lattice thereby disrupting the host lattice.

2. Experimental section

2.1. Chemicals

Bismuth(III) acetate (Bi(OAc)3, 90%, Aldrich), Se powder (99%, 100 mesh, Aldrich), copper(II) chloride dihydrate (CuCl2·2H2O), tetrakis(acetonitrile)copper(I) hexafluorophosphate (97%, Aldrich), oleylamine (OLAm, 70%, Aldrich), oleic acid (OLAc, 90%, Aldrich), octylamine (OctAm, 99%, Aldrich), octanoic acid (OctAc, 99%, Aldrich), 1-octadecene (1-ODE, 90%, Aldrich), tetrachloroethylene (TCE), chloroform, aceton, ethanol were used for the synthesis. All reactions were carried out under nitrogen atmosphere using Schlenk techniques unless otherwise stated.

2.2. Synthesis of Bi2Se3 nanosheets

To synthesis of Bi2Se3 nanosheets, first bismuth-oleate complex was prepared by dissolving 0.2 mmol of Bi(OAc)3 in a mixture of 500 μL OLAc, 500 μL OLAm, 500 μL OctAc, 500 μL OctAm and 1 ml of 1-ODE in a three neck round bottom flask at 100 °C. Formation of bismuth oleate complex results in a light yellow reaction colour. In a separate three neck round bottom flask, Se-complex was prepared by adding 0.3 mmol of Se powder in mixture of 2 ml OLAc, 2 ml OLAm, 500 μL OctAc, 500 μL OctAm and 1 ml of 1-ODE. The reaction mixture was heated to 180 °C and annealed for 60 min at the same temperature till a dark orange colour appears. The formation of dark orange colour ensures the complete dissolution of Se powder and formation of Se-complex. Then, initially prepared bismuth complex solution was swiftly injected into the Se-complex solution at 180 °C.
After annealing for 5 min at 180 °C, the reaction flask was rapidly cooled down to room temperature by using water bath. As synthesized Bi₃Se₅ nanosheets was precipitated out from the mixture using ethanol as antisolvent. Then, the solution was centrifuged at 5000 rpm to collect the precipitate and supernatant solution was discarded. Precipitate was washed with a mixture of chloroform and ethanol for three times. Finally, it was dispersed in toluene and stored for further use.

2.3. Synthesis of copper intercalated bismuth selenide nanosheets

2.3.1. Zero-valent copper (Cu⁰) intercalation:
Cu⁰ intercalated Bi₂Se₃ nanosheets was prepared by adding copper precursor solution into the Bi₂Se₃ nanosheets dispersion in toluene under stirring condition. Tetrakis(acetonitrile)copper(I) hexafluorophosphate was used as a copper precursor. Copper precursor solution was prepared by dissolving 6 mg of tetrakis(acetonitrile)copper(I) hexafluorophosphate in 4 ml methanol. Bi₂Se₃ nanosheets stock solution was prepared by dispersing the whole precipitate obtained from the synthesis of Bi₂Se₃ nanosheets in 2 ml toluene. 100 μl of this Bi₂Se₃ nanosheets dispersion was taken in a glass vial with 1 ml toluene and stirred well with a magnetic bar. 500 μl copper precursor solution in methanol was added to the Bi₂Se₃ nanosheets dispersion and stirred for 30 min. After 30 min of stirring, the reaction product was precipitated out using excess methanol and centrifugation at 3000 rpm. As obtained Cu⁰-Bi₂Se₃ nanosheets was then dispersed in toluene for further use. Percentage of Cu⁰ intercalation within the Bi₂Se₃ nanosheets was controlled by adjusting the amount of copper precursor during the intercalation reaction. Cu⁰-Bi₂Se₃ nanosheets was obtained via intercalation reaction using tetrakis(acetonitrile)copper(I) hexafluorophosphate with 5%, 10%, 30% and 60% compared to Bi₂Se₃ (molar ratio of copper precursor with respect to Bi₂Se₃ nanosheets). The reaction product obtained by using tetrakis(acetonitrile)copper(I) hexafluorophosphate with 5%, 10%, 30% and 60% are named as 5Cu-Bi₂Se₃, 10Cu-Bi₂Se₃, 30Cu-Bi₂Se₃ and 60Cu-Bi₂Se₃.

2.3.2. Mono-valent copper (CuI) substitution
Cu¹ substituted Bi₂Se₃ nanosheets was synthesized by injecting the copper precursor solution directly into the reaction solution of crude Bi₂Se₃ nanosheets at high temperature. Here crude Bi₂Se₃ nanosheets obtained after the reaction was used without purification. Copper precursor solution was prepared by dissolving 50 mg of CuCl₂, 2H₂O in a mixture of 1 ml OLA, 500 μl OctAm and 1 ml 1-ODE at 150 °C to form the Cu-ammine complex. This Cu-ammine complex solution was injected into the crude Bi₂Se₃ nanosheets at 180 °C and annealed for 5 min. Aliquots are taken at different time interval to monitor the progress of the reaction.

2.4. Characterization
Powder XRD measurements were carried out using Bruker D8 powder diffractometer with Cu Kα (λ = 1.54 Å) as the incident radiation. Thin film of the Bi₃Se₅ nanosheets was used for the XRD measurements. Thin film was prepared by drop casting the Bi₃Se₅ nanosheets on glass substrate. Transmission electron microscopy (TEM) was performed using UHR-FEG-TEM, JEOL; JEM 2100 F model operating at 200 kV. Size of Bi₂Se₃ NCs was analysed using Digital Micrograph (DM3) software from JEOL. Bi₂Se₃ NCs size was estimated by drawing line profile on the TEM image of NCs. Size distribution histogram plot was obtained by measuring the size of more than 100 Bi₂Se₃ nanoparticles. Lattice spacings of Bi₂Se₃ nanosheets were calculated from the HRTEM images of Bi₂Se₃ nanosheets by using the line profile tool of DM3 software. Selected area electron diffraction (SAED) and energy dispersive x-ray spectroscopy (EDX) were also measured with the same electron microscope. Raman spectra were recorded using a J-Y HORIBA T64000 triple Raman spectrophotometer. UV–vis–NIR absorption spectra were measured using Varian Carry 5000 UV–vis–NIR spectrophotometer. Atomic force microscopy (AFM) imaging of the Bi₂Se₃ nanosheets on a mica substrate was performed with an Asylum Research MFP-3D AFM in tapping mode using AC160TS silicon probes with nominal tip radii <10 nm. X-ray photoelectron spectroscopy (XPS) was carried out using Omicron x-ray photoelectron spectrometer with an Al Kα x-ray source.

3. Results and discussion

3.1. Preparation of Bi₃Se₅ nanosheets
Layered Bi₃Se₅ possess rhombohedral crystal structure with five atoms in one-unit cell [space group D₅₃d (R-3m)] (figure 1(a)) [43]. In rhombohedral Bi₃Se₅ crystal structure, the Bi and Se hexagonal planes remain in close stacked configuration with a repetition of every five atomic layers as Se(Bi)–Bi–Se(Bi)–Bi–Se(Bi) (figure 1(a)). The five-atom layers, known as quintuple layers (QLs), are arranged along the c-direction [34, 35]. The coupling between two atomic layers within one QL is strong, however, is much weaker in between two QLS, where the interaction is predominantly van der Waals type. Hence, crystalline Bi₃Se₅ can be exfoliated as 2D nanosheets.
similar to the graphene from bulk graphite. Additionally, guest atoms can be accommodated within the van der Waals gap between two QLs\cite{35}. The TEM image of as-synthesized Bi$_2$Se$_3$ nanosheets shows micrometer long dimension and a narrow thickness (figure 1(b)). High-resolution TEM (HRTEM) image of nanosheets reveals clear lattice fringes implying single-crystalline nature of the nanosheets (figure 1(c)). HRTEM image shows well-resolved lattice spacing of 0.35 ± 0.02 nm, which corresponds to the (101) planes of bulk rhombohedral Bi$_2$Se$_3$ (figure 1(c)). Selected area electron diffraction (SAED) pattern of Bi$_2$Se$_3$ nanosheets shows diffraction spots corresponding to (101), (110), (1110) and (1116) crystallographic planes of the rhombohedral structure (JCPDS #12-0732) (figure 1(d)). SAED analysis is in-line with the HRTEM and fast Fourier transformation image (inset, figure 1(c)). Energy-dispersive x-ray spectroscopy (EDX) shows elemental ratio of 38:62 of Bi:Se supporting an empirical formula of Bi$_2$Se$_3$ (figure S1, supporting information is available online at stacks.iop.org/MRX/6/124005/mmedia).

Most of the reported methods on the synthesis of Bi$_2$Se$_3$ NCs relied on the solvothermal method, where tuning of size, shape and composition appears to be challenging\cite{43}. We have synthesized Bi$_2$Se$_3$ nanosheets using colloidal route by rapid injection of bismuth-complex precursor to selenium-complex precursor in presence of high boiling solvents and capping ligands at 180 °C. Bismuth acetate was dissolved in pure oleic acid (OLAc) by heating the mixture above 150 °C\cite{44}. At this high temperature, there remains a possibility of formation of metallic Bi NCs or bismuth oxide which can be identified by visualizing the clear reaction solution into a black turbid medium\cite{44, 45}. This unwanted reaction product may affect the reaction kinetics and the morphology of the final product. Hence, we have prepared bismuth complex precursor at a relatively low temperature (100 °C) with the aid of mixture of short chain octanoic acid (OctAc) and octylamine (OctAm) ligands along with OLAc. Reactivity of Se towards different metal salts depends on the nature of Se precursor solution used in the reaction\cite{46}. Different Se precursors have been used so far to synthesize a variety of metal selenide NCs\cite{47}.

The use of Se-thiol precursor for the synthesis of bismuth chalcogenides induces immediate formation of metal sulphide NCs below 200 °C\cite{48}. Oleylamine (OLAm) and OLAc induced Se dissolution requires much higher reaction temperature above 300 °C\cite{49, 50}. High temperature dissolution of Se also leads to the formation of small Se NCs\cite{46}. OLAm induced heating of Se powder does not lead to the complete dissolution of Se even at high temperature\cite{51}. In contrary these literatures, our synthesis route is novel since we have used a combination of four ligands (OLAm, OLAc, OctAm, OctAc) along with non-coordinating solvent octadecene to dissolve Se at relatively low temperature (180 °C). Injection of Bi-complex into Se-complex leads to immediate

Figure 1. (a) Schematic presentation of atomic arrangement in a layered of Bi$_2$Se$_3$ with rhombohedral crystal structure. One quintuple layer (QL) is marked by the bracket. Blue and red spheres represent Bi and Se atoms respectively. (b) TEM image of Bi$_2$Se$_3$ nanosheets. (c) HRTEM image of the Bi$_2$Se$_3$ nanosheets showing lattice planes related to rhombohedral Bi$_2$Se$_3$ crystal structure. Inset shows the FFT pattern obtained from of the corresponding HRTEM. (d) SAED pattern of the Bi$_2$Se$_3$ nanosheets showing diffraction spots of rhombohedral Bi$_2$Se$_3$ crystal structure.
formation of Bi$_2$Se$_3$ nanostructures. TEM study of aliquot collected at different time interval after injection of Bi precursor into Se precursor shows formation of small Bi$_2$Se$_3$ NCs at the beginning of the reaction (figure 2).

TEM image of the aliquot taken after 10 s of the Se precursor injection shows the formation of Bi$_2$Se$_3$ NCs (figure 2(a)). Size distribution histogram shows that as obtained Bi$_2$Se$_3$ NCs have an average size of $\sim 2.5$ nm (figure 2(a), inset). TEM image of the aliquots collected at 1 min and 2 min of annealing reveal the coexistence of both Bi$_2$Se$_3$ NCs and nanosheets (figures 2(b), (c)). Size distribution histogram reveals that the Bi$_2$Se$_3$ NCs have an average size of $\sim 2.9$ nm for 1 min anneal sample (figure 2(b), inset). However, the TEM image of the aliquot collected at 5 min of annealing shows only Bi$_2$Se$_3$ nanosheets with large planar area (figure 2(d)). These observations reveal a fast formation of the single-crystalline Bi$_2$Se$_3$ nanosheets with large planar area, which occurs via 2D oriented attachment of small Bi$_2$Se$_3$ NCs followed by epitaxial recrystallization process[32].

X-ray diffraction (XRD) pattern of the Bi$_2$Se$_3$ nanosheets shows major reflection peaks corresponding to the (006), (101), (015) and (110) planes of the rhombohedral crystal structure of bulk Bi$_2$Se$_3$ (figure 3(a)). XRD pattern of the Bi$_2$Se$_3$ nanosheets obtained at different annealing time at 180 °C reveals that phase pure Bi$_2$Se$_3$ NCs is formed from the beginning of the reaction (Figure S2, supporting information). We have estimated the thickness of the as-synthesized Bi$_2$Se$_3$ nanosheets from the AFM topography image captured using tapping mode (figure 3(b)).
The AFM height profile shows a thickness $\sim$ 5 nm of nanosheets (inset, figure 3(b)) including the surface attached ligands on the both the top and bottom planes of the nanosheets [10]. Considering the geometric length of the surface attached ligands (OLAc, OLAm, OctAc, OctAm), the actual thickness of inorganic core of the nanosheet can be estimated to be $\sim$ 2 nm which corresponds to 2 QLs thickness [10, 43].

Selective insertion of copper (Cu$^0$ or Cu$I$) into the Bi$_2$Se$_3$ nanosheets can be achieved by treating the as-prepared Bi$_2$Se$_3$ nanosheets with a suitable copper precursor in an appropriate reaction condition. This can be achieved by treating Bi$_2$Se$_3$ nanosheets by Cu$I$ salt at room temperature or by injecting hot Cu$I$-amine complex into the reaction medium at high temperature. We have adopted both the reaction routes for selective insertion of copper (Cu$^0$ or Cu$I$) into the Bi$_2$Se$_3$ nanosheets. We observed that the use of Cu$I$-salt at room temperature leads to the formation of Cu$I$ intercalated Bi$_2$Se$_3$ nanosheets. Whereas, the use of Cu$I$-amine complex results in the formation of Cu$I$ substituted Bi$_2$Se$_3$ nanosheets at high temperature reaction. We have systematically studied the Cu$I$ intercalation and Cu$I$ substitution into the Bi$_2$Se$_3$ nanosheets using reaction processes both at room and high temperatures.

3.2. Preparation of Cu$^0$-Bi$_2$Se$_3$ nanosheets

For intercalation zero-valent metal into the layered materials various metal salts have been used which undergoes disproportionation reaction to yield zero-valent metal [34]. However, disproportionation reaction of metal salt depends on the stability of oxidation states of the corresponding metal ion, which depends on the types of metal. Mono-valent copper tends to disproportionate in solution following to the equation

$2\text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Cu}^0 + \text{Cu}^{2+}(\text{aq})$

The resulting Cu$^{2+}$ remains in the solvent as complex, thus releasing Cu$^0$ in dilute solution [41]. For a typical disproportionation reaction, the NCs, copper salt and solvent are taken into a reaction medium and heated just below reflux temperature. However, heating the reaction close to boiling point temperature of the solvent often damages the morphology of the NCs [42]. We have adopted modified method for disproportionation reaction for intercalation of copper atom into the Bi$_2$Se$_3$ nanosheets in comparison to the previous reports [30, 31, 34, 53]. We performed the reaction at room temperature using two partially immiscible solvents, toluene and methanol, which is advantageous in controlling the rate of intercalation of Cu$^0$ into the Bi$_2$Se$_3$ nanosheets. We have used air-stable Cu$I$ salt, tetrakis(acetonitrile)copper(I) hexafluorophosphate in toluene and methanol, which undergoes disproportionation redox reaction generating zero-valent copper. As discussed earlier, in the rhombohedral crystal lattice of Bi$_2$Se$_3$ nanosheets, the hexagonal planes of Bi and Se are closely stacked along the c-axis with every five repeat atomic layers in a sequence Se1--Bi--Se2--Bi--Se3 forming QLs. The van der Waals gap between two neighbouring Se layers is $\sim$2.6 Å, which is larger than the radius of a Cu$^0$ (1.28 Å) ion [54]. This makes Bi$_2$Se$_3$ nanosheets ideal host for the intercalation of zero-valent copper. The amount of zero-valent copper intercalation was controlled by tuning the duration of intercalation and the concentration of copper precursor salt relative to Bi$_2$Se$_3$ nanosheets (see experimental section) [30, 31, 34, 53]. Figure 4(a) shows the TEM images of Cu$^0$-Bi$_2$Se$_3$ nanosheets synthesized using 10% tetrakis(acetonitrile)copper(I) hexafluorophosphate (molar percentage). Pristine Bi$_2$Se$_3$ nanosheets in toluene were treated with methanolic solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate for zero-valent Cu$^0$ intercalation. The TEM image reveals that the morphology of nanosheets remain the same with the pristine Bi$_2$Se$_3$ nanosheets upon zero-valent copper intercalation (figure 4(a)).

Notably, the use of higher concentration of tetrakis(acetonitrile)copper(I) hexafluorophosphate results in the distortion of the morphology of the pristine nanosheets (figure S3, supporting information). HRTEM image (figure 4(b)) of Cu$^0$-Bi$_2$Se$_3$ nanosheets shows lattice spacings of 0.35 $\pm$ 0.02 nm similar to pristine Bi$_2$Se$_3$ nanosheets, which corresponds to the (101) planes of bulk rhombohedral Bi$_2$Se$_3$ (JCPDS # 12-0732). SAED pattern (figure 4(c)) of Cu$^0$-Bi$_2$Se$_3$ nanosheets shows diffraction spots similar to the pristine Bi$_2$Se$_3$ nanosheets. These results imply that the inherent crystal structure of the Bi$_2$Se$_3$ nanosheets remains unaltered with Cu$^0$ intercalation. EDX analysis (figure 4(d)) shows the atomic percentage of Cu:Bi:Se of 12:38:50 supporting intercalation of copper into the Bi$_2$Se$_3$ nanosheets. We have extracted the chemical oxidation states of Cu, Bi and Se of the Cu$^0$-Bi$_2$Se$_3$ nanosheets using XPS (figure 5). Comparison of the XPS spectra of pristine Bi$_2$Se$_3$ nanosheets with Cu$^0$-Bi$_2$Se$_3$ nanosheets reveals the effect of copper intercalation into the Bi$_2$Se$_3$ nanosheets. High-resolution XPS spectrum of pristine Bi$_2$Se$_3$ for Bi 4$f$ shows peaks at 157.3 and 162.6 eV with a splitting of 5.3 eV, which correspond to the Bi 4 $f_{7/2}$ and Bi 4 $f_{5/2}$ respectively (figure 5(a)).

The position of the both Bi 4$f_{7/2}$ and Bi 4$f_{5/2}$ peaks are shifted slightly (0.2 eV) to the higher binding energies of 157.5 and 162.8 eV respectively for Cu$^0$-Bi$_2$Se$_3$ nanosheets in comparison to the pristine Bi$_2$Se$_3$ (figure 5(a)). XPS spectrum of Se 3d of Bi$_2$Se$_3$ nanosheets is broad and asymmetric in nature, which is deconvoluted into two peaks (Figure S4, supporting information). One peak appears at binding energy of 53.1 eV corresponding to the Se 3d$_{5/2}$ and the other peak appears at binding energy of 54 eV related to Se 3d$_{3/2}$ (figure 5(b)). The XPS match well with the reported Bi$_2$Se$_3$ nanostructures [34, 35]. Cu$^0$-Bi$_2$Se$_3$ nanosheets show similar XPS spectrum of Se 3d orbital, however, is shifted about 0.7 eV towards higher binding energy compared to pristine Bi$_2$Se$_3$.
The XPS results show that both the Se 3d and Bi 4f peaks are shifted to higher binding energies upon Cu⁰ intercalation suggesting a modified charge density distribution in Cu⁰-Bi₂Se₃ nanosheets [53, 55]. XPS spectrum of Cu 2p orbital of Cu⁰-Bi₂Se₃ nanosheets shows doublet peaks for 2p₃/2 and 2p₁/₂ at binding energies of 932.2 eV and 952.2 eV respectively with a separation of 20.0 eV (figure 5(c)). The absence of any characteristic satellite peak in between the 2p₃/2 and 2p₁/₂ peaks suggests the nonexistence of mono-valent or di-valent states (Cu⁺ or Cu²⁺) in Cu⁰-Bi₂Se₃ nanosheets [30]. The XPS analyses confirm the successful intercalation of Cu⁰ within the Bi₂Se₃ nanosheets [34, 35].

Furthermore, we have carried out powder XRD measurements Cu⁰-Bi₂Se₃ nanosheets synthesized with the different amount of Cu⁰ and compared with the pristine Bi₂Se₃ nanosheets (figure 6(a)). XRD peaks for Cu⁰-Bi₂Se₃ nanosheets and pristine Bi₂Se₃ nanosheets appear in the same position for Cu⁰ intercalation till 30% suggesting that the host lattice of Bi₂Se₃ nanosheets remains unaltered till 30% of Cu⁰ intercalation. Lower amount of Cu⁰ can intercalate in the van der Waals gap between the QLs (figure S5, supporting information). However, a shift towards higher angles is observed for Cu⁰-Bi₂Se₃ nanosheets with 60% of Cu⁰-intercalation (figure 6(a)). This observation indicates a change in the lattice spacings for high densities of Cu⁰ intercalation. As
mentioned earlier, the use of larger amount of Cu$^0$ intercalation into Bi$_2$Se$_3$ nanosheets also changes the shape of the nanosheets (figure S3, supporting information). The intercalation of Cu$^0$ in larger volume causes the lattice contraction, which is in-line observed shift of the XRD peaks towards higher angles. The distortion of lattice may be attributed to a wide range of factors including the volume of the intercalants and the electrostatic interactions between the host Bi$_2$Se$_3$ nanosheets and guest Cu$^0$ intercalants [34]. UV–vis-NIR absorption spectrum of Bi$_2$Se$_3$ nanosheets shows a broad absorption with a peak at 700 nm (figure S6, supporting information). UV–vis-NIR absorption spectra of Cu$^0$-Bi$_2$Se$_3$ nanosheets show the same absorption peak till 30% Cu$^0$ intercalation (figure S6, supporting information). However, a blue shift to 130 nm is observed for the Cu$^0$-Bi$_2$Se$_3$ nanosheets with 60% of Cu$^0$ intercalation. The observed blue shift of the absorption peak may be attributed to the observed contraction of lattice spacing of the pristine Bi$_2$Se$_3$ nanosheets with larger amount of Cu$^0$ intercalation.

The UV–vis-NIR absorption spectrum of Bi$_2$Se$_3$ nanosheets shows a broad absorption with a peak at 700 nm (figure S6, supporting information). UV–vis-NIR absorption spectra of Cu$^0$-Bi$_2$Se$_3$ nanosheets show the same absorption peak till 30% Cu$^0$ intercalation (figure S6, supporting information). However, a blue shift to 130 nm is observed for the Cu$^0$-Bi$_2$Se$_3$ nanosheets with 60% of Cu$^0$ intercalation. The observed blue shift of the absorption peak may be attributed to the observed contraction of lattice spacing of the pristine Bi$_2$Se$_3$ nanosheets with larger amount of Cu$^0$ intercalation.

The Raman spectrum of bulk Bi$_2$Se$_3$ exhibits prominent peaks at 72 cm$^{-1}$, 131 cm$^{-1}$, and 174 cm$^{-1}$, which are assigned to A$_1g$, E$_g$, and A$_2g$ modes respectively [36, 57]. Bi$_2$Se$_3$ nanosheets also show two A$_{1g}$ modes at ~69.38 and ~172.87 cm$^{-1}$ and an E$_g$ mode at ~129.95 cm$^{-1}$ (figure 6(b)). We found that all the peaks are shifted to lower wavenumber by ~2 cm$^{-1}$ (figure 6(b)) for Bi$_2$Se$_3$ nanosheets in comparison to the bulk Bi$_2$Se$_3$ [34]. The A$_{1g}$ modes correspond to the out-of-plane vibrations parallel to the c-axis and the E$_g$ phonon mode corresponds to in-plane bond vibrations perpendicular to the c-axis (figure 6(c)) [34, 56, 57]. Hence, A$_{1g}$ mode is more sensitive to thickness since it reflects the out-of-plane vibrations of the Se and Bi atoms, [56] and the interlayer van der Waals interactions influence the effective restoring forces acting on these atoms. The observed shift can be attributed to the lower degree of the in-plane and out-of-plane vibrations in the nanosheets compared to the bulk Bi$_2$Se$_3$ [57]. Cu$^0$-Bi$_2$Se$_3$ nanosheets exhibits similar Raman active phonon modes (A$_{1g}$, A$_{1g}$, and E$_g$) like Bi$_2$Se$_3$ nanosheets (figure 6(b)). This observation indicates that intercalated Cu$^0$ forms non bonding interaction with the host Bi$_2$Se$_3$ nanosheets since any bonding would have affected the phonon modes. Additionally, Cu$^0$
adopted the cation exchange method to form CuI-Bi2Se3 nanosheets by using oleylamine complex of copper. This observation also suggests that the intercalated copper remains in zero-valent character. This observation further supports the intercalation does not show any new peak in the Raman spectrum owing to the infinitely polarisable nature. This confirms that intercalated Cu0 remains within the QLs of Cu0-Bi2Se3 nanosheets rather than substituting Bi cations from the Bi2Se3 lattice.

3.3. Preparation of CuI-Bi2Se3 nanosheets
CuI substituted Bi2Se3 nanosheets (CuI-Bi2Se3 nanosheets) were synthesized by injecting hot Cu(I)-oleylamine precursor solution into the pre-synthesized Bi2Se3 nanosheets at 180 °C. Cation or anion exchange route of the pre-synthesized NCs is advantageous since the shape of the resultant NCs can be retained[58, 59]. We have adopted the cation exchange method to form CuI-Bi2Se3 nanosheets by using oleylamine complex of copper which controls the rate of exchange reaction.

TEM image shows that the morphology of pristine Bi2Se3 nanosheets remains the same after CuI substitution (figure 7(a)). HREM image shows lattice spacings of 0.40 ± 0.02 nm which corresponds to the (101) planes of rhombohedral Bi2Se3 crystal structure (JCPDS # 12-0732, figure 7(b)). This reveals that lattice spacing of (101) plane increase after CuI substitution in comparison to 0.35 ± 0.02 nm for pristine Bi2Se3 nanosheets. SAED pattern also shows diffraction spots corresponding to the (101) planes of the rhombohedral Bi2Se3 (figure 7(c)). EDX analysis also reveals that the atomic ratio of Cu:Bi:Se for CuI-Bi2Se3 nanosheets is 15:29:56 respectively.

Notably, the absorption spectrum of CuI-Bi2Se3 nanosheets appears different from the absorption spectra of Cu0-Bi2Se3 or pristine Bi2Se3 nanosheets. The XPS spectrum of CuI-Bi2Se3 nanosheets for Se 3d orbital shows a broad nature and is shifted towards higher energy of 1.1 eV in comparison to pristine Bi2Se3 nanosheets. Additionally, completely new peaks appear for longer annealing time, which corresponds to the reflection planes of Cu2-Se (JCPDS # 03-065–1656) [60]. This observation confirms that CuI completely substitutes BiIII of Bi2Se3 nanosheets at longer annealing time to yield a phase transition to Cu2-Se NCs.

Injection of CuI-oleylamine precursor to host Bi2Se3 nanosheets initiates partial substitution of BiIII at the beginning of the reaction, which in turn gradually replaces BiIII at longer annealing time. We have compared the XPS spectra of CuI-Bi2Se3 nanosheets with the Bi2Se3 nanosheets. The XPS spectrum of CuI-Bi2Se3 nanosheets for Bi 4f orbital shows that the Bi 4f7/2 and Bi 4f5/2 peaks are shifted towards higher binding energy compared to pristine Bi2Se3 nanosheets (figure 8(c)). The XPS spectrum of CuI-Bi2Se3 nanosheets for Se 3d orbital shows a broad nature and is shifted towards higher energy of 1.1 eV in comparison to pristine Bi2Se3 nanosheets (figure 8(d)). XPS analysis of Cu 2p orbital of CuI-Bi2Se3 nanosheets shows doublet peaks of Cu 2p3/2 and Cu 2p1/2 at binding energies of 932 eV and 952 eV respectively (figure 8(e)). Interestingly, a low intensity satellite peak marked by blue asterisk appears in between the Cu 2p3/2 and Cu 2p1/2 peaks at a binding energy of 944 eV (figure 8(e)). The satellite peak was absent in case of Cu0-Bi2Se3 nanosheets or pristine Bi2Se3 nanosheets (figures 5(c) and S9c, supporting information).

The appearance of the low intensity satellite peak confirms the presence of CuI oxidation state within the CuI-Bi2Se3 nanosheets [34, 35]. These observations indicate that CuI interacts with the host Bi2Se3 nanosheets by replacing bismuth ion to form CuI-Bi2Se3 nanosheets.

Figure 7. (a) TEM images of CuI-Bi2Se3 nanosheet synthesized by injecting of CuI into the Bi2Se3 nanosheet at 180 °C with annealing time of 10 s. (b) HRTEM of CuI-Bi2Se3 nanosheet showing (101) lattice planes of Bi2Se3 nanosheet. (c) SAED pattern of CuI-Bi2Se3 nanosheet.
The Raman spectrum of CuI-Bi2Se3 nanosheets exhibits prominent peaks at 70 cm⁻¹, 129.5 cm⁻¹, and 175 cm⁻¹ corresponding to A₁g, E₂g, and A₁g modes respectively (figure 9). The out-of-plane phonon mode A₁g and in-plane mode E₂g show almost similar peak positions compared to the pristine Bi2Se3 nanosheets (figure 9(a)). However, the out-of-plane phonon mode A₁g shows a shift to longer wavenumber compared to A₁g mode of pure Bi2Se3 nanosheets (figure 9(a)). The bonding interaction between the mono-valent copper and host Bi2Se3 nanosheets clearly affects the out-of-plane phonon modes.

This observation also indicates towards the cation substitution of Bi2Se3 nanosheets by CuI, which is in sheer contrast with the Cu⁰-Bi2Se3 nanosheets with Cu⁰ intercalation. Raman spectra with different annealing time show a gradual shift of the A₁g peak of CuI-Bi2Se3 nanosheets to longer wavenumber in comparison to the Bi2Se3 nanosheets (figure 9(b)). Raman spectra with different annealing time also confirm Bi⁰ substitution by Cu¹ into the Bi2Se3 nanosheets. Prominent peaks of pristine Bi2Se3 tends to disappear for CuI-Bi2Se3 nanosheets at 5 min.
annealing time. This observation is in-line with the XRD analyses which revealed the appearance of Cu$_{2-x}$Se phase at 5 min of annealing.

4. Conclusions

In conclusion, large area and ultrathin 2D Bi$_2$Se$_3$ nanosheets are synthesized using colloidal synthesis method. Formation and growth mechanism of Bi$_2$Se$_3$ nanosheets reveals oriented attachment of small Bi$_2$Se$_3$ NCs followed by epitaxial recrystallization to form single-crystalline nanosheets. We have systematically studied the Cu$^0$ intercalation and Cu$^+$ substitution into the Bi$_2$Se$_3$ nanosheets by choosing appropriate reaction conditions. Selective intercalation of copper Cu$^0$ into the van der Waals gap between two QLs of Bi$_2$Se$_3$ nanosheets was achieved by treating the as-prepared Bi$_2$Se$_3$ nanosheets with Tetrakis(acetonitrile)copper(I) hexafluorophosphate as copper precursor at room temperature. The Cu$^0$ intercalated Bi$_2$Se$_3$ nanosheets show similar structural and optical properties like pristine Bi$_2$Se$_3$ nanosheets. However, intercalated Cu$^0$ in between the adjacent layers of Bi$_2$Se$_3$ nanosheets can be beneficial for supercapacitor applications and fast ionic transport through the 2D channels. On the other hand, the use of Cu$^+$-amine complex results in the formation Cu$^+$ substituted Bi$_2$Se$_3$ nanosheets at high temperature reaction conditions. Cu$^+$ substituted Bi$_2$Se$_3$ nanosheets was obtained at the shorter reaction time while a complete cation exchange reaction leads to the formation of Cu$_{2-x}$Se phase. The development of new synthetic strategy for the synthesis of 2D shape-controlled Bi$_2$Se$_3$ nanosheets and understanding the role of metal ion intercalation or substitution are important for fundamental understanding and energy related applications.

Acknowledgments

We acknowledge SERB grant EMR/2014/000664, DST, India, for financial support. D Roy and S Paul acknowledge UGC, India for research fellowship.

ORCID iDs

Somobrata Acharya © https://orcid.org/0000-0001-5100-5184

References

[1] Yin Y and Alivisatos A P 2005 Colloidal nanocrystal synthesis and the organic-inorganic interface Nature 437 664–70
[2] Nurmikko A 2015 What future for quantum dot-based light emitters? Nat. Nanotechnol. 10 1001–4
[3] Kovalenko M V 2015 Opportunities and challenges for quantum dot photovoltaics Nat. Nanotechnol. 10 994–7
[4] Talapin D V, Lee J-S, Kovalenko M V and Shevchenko E V 2010 Prospects of colloidal nanocrystals for electronic and optoelectronic applications Chem. Rev. 110 389–458
[5] Brucher M, Moronne M, Gin P, Weiss S and Alivisatos A P 1998 Semiconductor nanocrystals as fluorescent biological labels Science 281 2013–6
[6] Dalui A, Khan A H, Pradhan B, Pradhan J, Satpati B and Acharya S 2015 Facile synthesis of composition and morphology modulated quaternary CuZnFeS colloidal nanocrystals for photovoltaic application RSC Adv. 5 97465–94
[7] Khan A H, Pal S, Dalui A, Pradhan B, Sarma D D and Acharya S 2019 Tuning copper sulfide nanosheets by cation exchange reactions to real two-dimensional CZTS dielectric layers Journal of Materials Chemistry A 7 9782–90
[8] Dalui A, Pandey M, Sarkar P K, Pradhan B, Vasdev A, Manik N B, Sheet G and Acharya S 2019 Realization of diverse waveform converters from a single nanoscale lateral p–n Junction Cu$_x$S–CdS Heterostructure ACS Applied Materials & Interfaces 11 11749–54
[9] Dalui A, Pradhan B, Thupakula U, Khan A H, Sandeep Kumar G, Ghosh T, Satpati B and Acharya S 2015 Insight into the mechanism revealing the peroxidase mimetic catalytic activity of quaternary CuZnFeS nanocrystals: colorimetric biosensing of hydrogen peroxide and glucose Nanoscale 7 9062–74
[10] Acharya S, Das B, Thupakula U, Ariga K, Sarma D D, Israelachvili J and Golan Y A 2013 Bottom-up approach toward fabrication of ultrathin PbS sheets Nano Lett. 13 409–13
[11] Aono M and Ariga K 2016 The way to nanoarchitectonics and the way of nanoarchitectonics Adv. Mater. 28 989–92
[12] Pradhan B, Sandeep Kumar G, Dalui A, Khan A H, Satpati B, Ji Q, Kumar Shrestha L, Ariga K and Acharya S 2016 Shape-controlled cobalt phosphide nanoparticles as volatile organic solvent sensor Journal of Materials Chemistry C 4 4967–77
[13] Pradhan B, Mushag A, Roy D, Sain S, Das B, Ghori U K, Pal S K and Acharya S 2019 Postsynthesis spontaneous coalescence of mixed-halide perovskite nanocubes into phase-stable single-crystalline uniform luminescent nanowires The Journal of Physical Chemistry Letters 10 1803–12
[14] Khan A H, Dalui A, Mukherjee S, Segre C U, Sarma D D and Acharya S 2015 Efficient solid-state light-emitting CuCdS nanocrystals synthesized in air Angew. Chem. Int. Ed. 54 2643–8
[15] Gao M-R, Jiang J and Yu S-H 2012 Solution-based synthesis and design of late transition metal chalcogenide materials for oxygen reduction reaction (ORR) Small 8 113–27
[16] Lai C-H, Lu M-Y and Chen L-J 2011 Metal sulfide nanostructures: synthesis, properties and applications in energy conversion and storage J. Mater. Chem. 22 19–30
[17] Feng Y and Alonso-Vante N 2008 Non precious metal catalysts for the molecular oxygen-reduction reaction physica status solidi (b) 245 1792–806
[18] Chen Z, Higgins D, Yu A, Zhang L and Zhang J 2011 A review on non-precious metal electrocatalysts for PEM fuel cells Energy & Environmental Science 4 3167–92
[19] Guin S N, Chatterjee A, Negi D S, Datta R and Biswas K 2013 High thermoelectric performance in tellurium free p-type AgSbSe2, Energy & Environmental Science 6 2603–8
[20] Khan A H, Ghosh S, Pradhan B, Dalui A, Shrestha L K, Acharya S and Ariga K 2017 Two-dimensional (2D) nanomaterials towards electrochemical nanoarchitectonics in energy-related applications Bull. Chem. Soc. Jpn. 90 627–48
[21] Muller G A, Cook J B, Kim H S, Tolbert S H and Dunn B 2015 High performance pseudocapacitor based on 2D layered metal chalcogenide nanocrystals Nano Lett. 15 1911–7
[22] Wang F, Tang R, Yu H, Gibbons P C and Buhro W E 2008 Size and shape controlled synthesis of bismuth nanoparticles Chem. Mater. 20 3656–62
[23] Mendoza-Sánchez B and Gogotsi Y 2016 Synthesis of two-dimensional materials for capacitive energy storage Adv. Mater. 28 6104–35
[24] Ubbelohde A R 1979 Intercalation compounds Intercalated Layered Materials 1–31 (Dordrecht: Springer)
[25] Gamble F R, DiSalvo F J, Klemm R A and Geballe T H 1970 Superconductivity in layered structure Organometallic Crystals Science 168 568–70
[26] Morosan E, Zandbergen H W, Dennis B S, Bos J W G, Onose Y, Klimczuk T, Ramirez A P, Ong N P and Cava R J 2006 Superconductivity in Cu3Te5 Nan. Phys. 2 544–50
[27] Weller T E, Ellerby M, Saxena S S, Smith R P and Skippner N T 2005 Superconductivity in the intercalated graphite compounds C6Yb and C6Ca Nat. Phys. 1 39–41
[28] Sididrov M V, McKelvy M J, Cowley J M and Glaunsinger W S 1998 Novel guest–layer behavior of mercury titanium disulfide intercalates Chem. Mater. 10 3290–9
[29] Gnan P, Moreau P, Ouvarov G, Sididrov M, McKelvy M and Glaunsinger W 1995 Structural investigation of mercury–intercalated titanium disulfide. I. The crystal structure of Hg89Te42 Chem. Mater. 7 1132–9
[30] Koski K J, Cha J J, Reed B W, Wessells C D, Kong D and Cui Y 2012 High-density chemical intercalation of zero-valent copper into Bi2Se3 nanoribbons JACS 134 2884–7857
[31] Yao J, Koski K J, Luo W, Cha J J, Hu L, Kong D, Narasimhan V K, Huo K and Cui Y 2014 Optical transmission enhancement through chemically tuned two-dimensional bismuth chalcogenide nanofilms Nano Lett. 15 1735–76
[32] Wang M and Koski K J 2013 Reversible chemochromic MoO3 nanoribbons through zerovalent metal intercalation ACS Nano 9 3226–33
[33] Thenuwar A et al 2015 Copper–intercalated birnessite as a water oxidation catalyst Langmuir 31 12807–13
[34] Chen K P, Chung F R, Wang M and Koski K J 2015 Dual element intercalation into 2D layered Bi2Se3 nanoribbons JACS 137 5431–7
[35] Koski K J, Wessells C D, Reed B W, Cha J J, Kong D and Cui Y 2012 Chemical intercalation of zerovalent metals into 2D layered Bi2Se3 nanoribbons JACS 134 13737–9
[36] Bernevig B A, Hughes T L and Zhang S C 2006 Quantum spin hall effect and topological phase transition in HgTe quantum wells Science 314 1757–61
[37] Zhang H, Liu C-X, Qi X-L, Dai X, Fang Z and Zhang S-C 2009 Topological insulators in Bi2Se3, Bi2Te3, and Sb2Te3 with a single Dirac cone on the surface Nat. Phys. 5 348–42
[38] Xia Y et al 2009 Observation of a large-gap topological–insulator class with a single Dirac cone on the surface Nat. Phys. 5 398–402
[39] Peng H, Lai K, Kong D, Meister S, Chen Y, Qi X-L, Zhang S-C, Shen Z-X and Cui Y 2010 Aharonov–Bohm interference in topological insulator nanoribbons Nat. Mater. 9 225–9
[40] Ipas P et al 2014 Observation of surface dirac cone in high-quality ultrathin epitaxial Bi2Se3 topological insulator on AlN(0001) Dielectric, ACS Nano 8 6614–9
[41] Mackay K M 2002 Introduction to Modern Inorganic Chemistry 6th ed. (Boca Raton, FL: CRC Press)
[42] Li M, Zhang X, Dong T, Wang P, Postolek K M and Yang P 2018 Evolution of morphology, phase composition, and photoluminescence of cesium lead bromine nanocrystals with temperature and precursors J. Phys. Chem. C 122 28968–76
[43] Min Y, moon G D, Kim B S, Lim B, Kim J-S, Kang C Y and Jeong U 2012 Quick, controlled synthesis of ultrathin Bi2Se3 nanodiscs and nanosheets JACS 134 2872–5
[44] Konstantatos G, Levina I, Tang L and Sargent E H 2009 Sensitive solution-processed Bi2S3 nanocrystalline photodetectors Nano Lett. 9 4002–6
[45] Loidice A, Cooper J K, Hess L H, Mattox T M, Sharp I D and Buonsanti R 2015 Assembly and photocarrier dynamics of heterostructured nanocomposite photoanodes from multicomponent colloidal nanocrystals Nano Lett. 15 7347–54
[46] Bullern C, Embelen J, van Jasienski J, Cosgriff E J, Mulder R J, Rizzardo E, Bouwstra and Raston C L 2010 High activity phosphine–free selenium precursor solution for semiconductor nanocrystal growth Chem. Mater. 22 4135–43
[47] Pu C, Zhou J, Lai R, Niu Y and Peng X 2013 Highly reactive, yet flexible green Se precursor for metal selenide nanocrystals: S–octadecene suspension (Se–SUS) Nano. Res. 6 652–70
[48] Patra B K, Khilaris B, Bera A, Meheretor S K, Pradhan D and Pradhan N 2017 Chemically filled and Au–Coupled Bi2S3 nanorod heterostructures for photocatalysis Nano Res. 10 29 29–37
[49] Wang X, Liu X, Yin D, Ke Y and Swihart M T 2015 Size-, shape-, and composition-controlled synthesis and localized surface plasmon resonance of copper tin selenide nanocrystals Chem. Mater. 27 3378–88
[50] Mouridioudis S and Liz-Marzán L M 2013 Oleylamine in nanoparticle synthesis Chem. Mater. 25 1465–76
[51] Liu Y, Yao D, Shen L, Zhang H, Zhang X and Wang D 2012 Bi2Al12Sb8 enabled se powder dissolution in oleylamine at room temperature for the phosphine-free synthesis of copper–based quaternary selenide nanocrystals JACS 134 7207–10
[52] Schliehe C et al 2010 Ultrathin PbS sheets by two-dimensional oriented attachment Science 329 530–3
[53] Zhang J, Sun J, Li Y, Shi F and Cui Y 2017 Electrochemical control of copper intercalation into nanoscale Bi2Se3 Nano. Lett. 17 1741–7
[54] Shannon R D 1976 Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides Acta Crystallographica section A: Crystal Physics, Diffraction, Theoretical and General Crystallography 32 751–67
[55] Luo P, Zhuo F, Zhang Q, Chen Y, Lv L, Huang Y, Li H and Zhai T 2013 Doping engineering and functionalization of two-dimensional metal chalcogenides Nanoscale Horizons 4 26–31
[56] Richter W and Becker C R 2006 A Raman and far-infrared investigation of phonons in the rhombohedral V2–V3 compounds Bi2Te3, Bi2Se3, Sb2Te3 and Bi2(Te1–xSex)x (0 < x < 1), (Bi1–xSb)yTe2Z (0 < y < 1), (Bi1–xSb)yTe2 and (Bi1–xSb)yTe2 Sb2Te3 and Bi2(Te1–xSex)x 0
[57] Zhang J, Peng Z, Soni A, Zhao Y, Xiong Y, Peng B, Wang J, Dresselhaus M S and Xiong Q 2011 Raman spectroscopy of few-quantum layer topological insulator Bi2Se3 nanoplatelets Nano Lett. 11 2407–14
[58] Xie Y et al 2013 Copper sulfide nanocrystals with tunable composition by reduction of covellite nanocrystals with Cu$^+$ ions JACS 135 17630–7
[59] Trizio D L and Manna L 2016 Forging colloidal nanostructures via cation exchange reactions Chem. Rev. 116 10852–87
[60] Trizio D L, Li H, Casu A, Genovese A, Sathya A, Messina G C and Manna L 2014 Sn cation valency dependence in cation exchange reactions involving Cu$_{2-x}$Se nanocrystals JACS 136 6277–16284