# Solvothermal synthesis and AFM characterization of $TiSe_2$ two-dimensional sheets

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***Abstract*— There are many Van der Waals solids that can be isolated into two-dimensional (2D) sheets. Since the isolation of graphene in 2004 by graphite exfoliation, the synthesis and characterization of these new materials have increased notably due to their exceptional physical properties, which is leading to great advances in different areas of science and technology. This work presents the solvothermal synthesis in hydrazine of 2D titanium diselenide ($TiSe_2$) sheets and its subsequent characterization by Atomic Force Microscopy (AFM). The synthesis process is carried out from $TiSe_2$ crystals, and treating a dispersion of them in a hydrazine at 180°C during three hours under pressure. The interaction between hydrazine and selenium atoms seems to be enough to overcome the van der Waals forces that hold the crystal together, producing exfoliation in single or few-layer sheets. AFM measurements show that sheets of (0.60 ± 0.08) nm thick are obtained, which is consistent with previous reports of $TiSe_2$ monolayers.**

**Keywords— $TiSe_2$, AFM, SPM, solvothermal synthesis, 2D materials**

## 1. INTRODUCTION

In van der Waals solids the atoms or molecules are linked in a two-dimensional structure, forming 2D sheets. These sheets interact with each other through van der Waals (vdW) forces to form a three-dimensional structure, as in graphite. To isolate single 2D sheets, these forces that hold the solid together must be overcome. This is a physical process, also known as exfoliation. Since the isolation of graphene in 2004 by graphite exfoliation, the synthesis and characterization of new two-dimensional (2D) materials has increased notably. This interest is based on the exceptional physical properties of these crystals, which is leading to great advances in different areas of science and technology [1].

Within two-dimensional crystals, 2D semiconductors such as transition metal dichalcogenides (TMDCs) are receiving great attention, particularly for the controlled synthesis of vdW heterostructures that allow multiple applications in the areas of photonics and energy [3][4]. These TMDCs are compounds of the MX2 form, where M is a transition metal and X is a chalcogen atom. In general, the synthesis of these 2D materials is carried out by chemical vapor deposition (CVD), mechanical exfoliation, and liquid phase exfoliation. This last one has clear advantages, especially if high throughput and high-volume processing is required [5].

The main objective of this work is to develop a liquid phase exfoliation method to efficiently produce 2D sheets which can be scaled up. The initial approach consists of an electrochemical pre-exfoliation, followed by a solvothermal exfoliation process using hydrazine ($N_2H_4$) as an intercalating solvent. In order to evaluate the method, $Cu_xTiSe_2$ crystals (x = 0.11, 0.064 and 0) will be used. To date this material has proven to be difficult to obtain as a monolayer by methods other than epitaxial growth [6]. $TiSe_2$ is a 2D crystal with a hexagonal structure as shown in Fig. 1.

The vdW interaction between adjacent sheets are the responsible of the 3D hexagonal crystal stability. These interactions are stronger between selenium atoms located in contiguous sheets. For this reason, if an external compound interacts with the selenium atoms, the Se-Se vdW forces can be overcome and the exfoliation process of the crystal into 2D sheets can take place. At first, the crystal will undergo an electrochemical treatment, where the production of $H_2$ at negative potentials (reduction) may acts as an intercalating agent. Subsequently, the pre-expanded material will be solvothermically treated under subcritical conditions where the hydrazine is expected to complete the exfoliation process. For the process to be successful, these compounds should interact with the selenium atoms producing exfoliation, without any chemical modification of the 2D crystal.

In order to characterize these 2D sheets and evaluate the success of the exfoliation method, an atomic resolution microscope is required to differentiate monolayers from multilayers. The atomic force microscopy (AFM) meets this requirement and is the most versatile technique for obtaining images with high resolution on the z axis. Further, AFM phase imaging in intermittent contact mode allows to distinguishing between materials of different nature due to their mechanical properties.

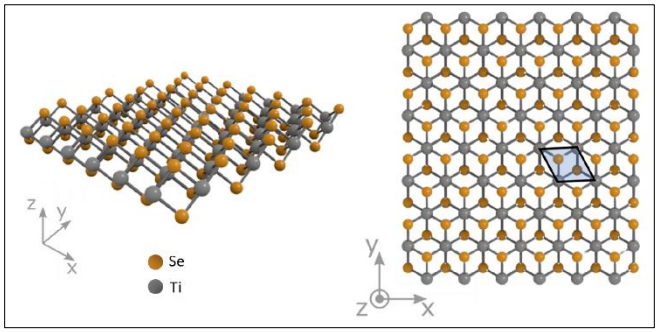


**Fig. 1.** Crystalline structure of a monolayer of titanium diselenide ($TiSe_2$). The Selenium atoms are shown as orange spheres, and those of Titanium as gray spheres. A hexagonal unit cell is also represented, which is defined by the parameters a = b = 0.354 nm, c = 0.601 nm, α = β = 90 °, γ = 120 °. Image adapted from [7].

## 2. METHODOLOGY

### 2.1. $TiSe_2$ CRYSTALS

The starting materials used in all the experiments were $Cu_xTiSe_2$ crystals synthesized by the standard iodine vapor transport method [8]. The crystals are labeled by 1, 2 and 5 in Fig. 2.

### 2.2. ELECTROCHEMICAL EXFOLIATION

Similar to the method developed for the exfoliation of graphite to obtain graphene [9], the process includes electrochemical treatment using potentiostatic and potentiodynamic methods in tetrahydrofuran (THF) or water containing perchloric acid ($HClO_4$) capable of producing $H_2$ by reduction. The synthesized material was purified by centrifugation using ultrapure water.

### 2.3. SOLVOTHERMAL EXFOLIATION

In order to exfoliate these crystals into 2D sheets, a solvothermal synthesis was carried out, placing the crystal in contact with hydrazine and then placed into an oven at 180°C during three hours. The exfoliation process is performed under subcritical conditions using an autoclave (Parr, modelo-4744) fitted with a 40_ml polytetrafluoroethylene PTFE container. A diagram of the reactor is shown in Fig. 3.

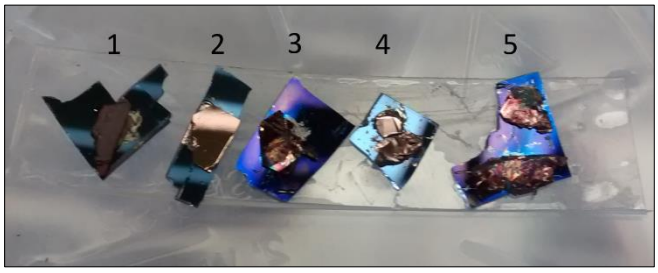


**Fig. 2.** 3D $TiSe_2$ crystals. They were synthesized by the group of Prof. Goran Karapetrov, Drexel University [10]. Crystal (1) is $Cu_xTiSe_2$, with x = 0.11; copper is found between the selenium atoms of contiguous sheets. The crystal (2) is pure $TiSe_2$. Crystals (3), (4) and (5) are $Cu_xTiSe_2$, with x = 0.064.

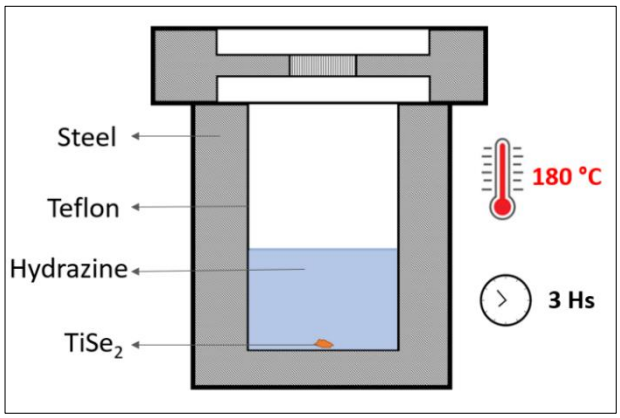


**Fig. 3.** Diagram of the reactor used for the solvothermal synthesis of $TiSe_2$ sheets. It is placed into an oven under subcritical conditions at 180 ° C for three hours, above the boiling point of hydrazine (114 ° C). These conditions increase the interaction between hydrazine and selenium atoms, accelerating the exfoliation process.

The material dispersed in hydrazine was then centrifuged to remove impurities and crystal fragments that were not exfoliated. The supernatant containing $TiSe_2$ sheets dispersed in hydrazine and water is stored at 5 °C in the absence of light until it is analyzed by AFM.

### 2.4. AFM MEASUREMENTS

For characterization by AFM, the solution is deposited by drop casting on freshly cleaved mica (an atomically flat substrate). Measurements are carried out using an Agilent SPM model 5500 working in acoustic AC mode. This mode allows to measure topography with great precision in the z-axis (necessary to determine the thickness of the isolated sheets) and simultaneously have a phase contrast image (due to different mechanical properties) which allows the $TiSe_2$ sheets to be distinguished from the substrate (mica).

## 3. RESULTS

### 3.1. ELECTROCHEMICAL EXFOLIATION

Initially, the electrochemical exfoliation $Cu_xTiSe_2$ crystals was attempted in a three-electrode cell. The exfoliation product, whether in aqueous or organic medium, using a potentiostatic method or by potential scanning, was analyzed by infrared spectroscopy (FTIR), showing clear signs of degradation, probably due to $Ti^{+4}$ reduction. In Fig. 4 the electrochemical cell and the product resulting from the exfoliation process are shown.

### 3.2. SOLVOTHERMAL EXFOLIATION

Hydrazine appears to be an efficient media to exfoliate $Cu_xTiSe_2$. In fact, after a few hours at room temperature and atmospheric pressure, a spontaneous expansion of the $TiSe_2$ crystal is observed. The subcritical conditions significantly accelerate the process and in three hours at 180 °C the absence of massive material in the reactor is visually noted. Subsequently, the exfoliated material is precipitated and purified by centrifugation, interchanging part of the hydrazine for water as the solvent (Fig. 5).

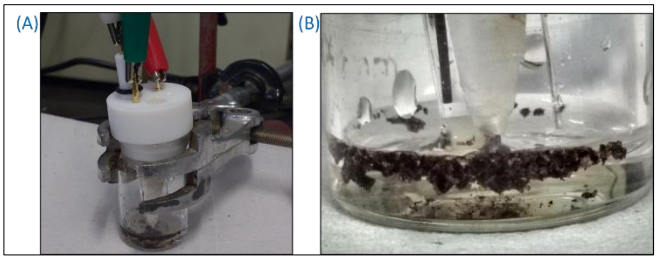


**Fig. 4.** (A) Electrochemical cell used in the experiments. $Cu_xTiSe_2$ was used as a working electrode and a Pt wire as a counter electrode and a normal hydrogen electrode (in aqueous medium) or an Ag wire (in THF) as a reference or pseudo-reference electrode, respectively. (B) Image of the expanded material after a reduction process.

### 3.3. AFM RESULTS - $Cu_{0.11}TiSe_2$ (CRYSTAL 1) AND $TiSe_2$ (CRYSTAL 2)

The hydrazine exfoliation process was applied on crystals 1 and 2 of Fig. 2., both under standard atmospheric and high temperature and pressure conditions.

The first crystal is doped with copper atoms, $Cu_{0.11}TiSe_2$. In this case, it can be observed that the expansion process occurs spontaneously under standard atmospheric conditions within a few hours after the crystal comes into contact with the solvent. The AFM images of both samples, those treated under ambient and subcritical conditions; show a high density of nanoparticles that prevent observing the $TiSe_2$ crystal

sheets. They are probably copper NPs, therefore, under these conditions the $TiSe_2$ sample is not easy to isolate to be characterized.

The $TiSe_2$ pure crystal, with no Cu as dopant (x = 0), requires treatment under subcritical conditions for its exfoliation; no expansion is visible under ambient pressure and temperature conditions. Topography measurements of the exfoliation product by AFM show a low density of 2D sheets, and the fragments found present heights between 3 and 8 nm as shown in Fig. 6. In other words, the crystal has not been fully exfoliated to obtain single sheets (~0.60 nm). This shows a low efficiency in the exfoliation process. Perhaps a longer treatment time is required to achieve a full exfoliation.

**Fig. 5.** Picture of the $TiSe_2$ crystal dispersion after solvothermal treatment in hydrazine at 180 °C for 3 hours. A dispersion is observed containing some macroscopic fragments at the bottom, which are eliminated by centrifugation.

### 3.4. AFM Results - $Cu_{0.065}TiSe_2$ crystal (5)

The exfoliation process from hydrazine was also carried out on crystal 5 of Fig. 2. Topography AFM images show that the approximate height of these sheets is 0.61nm, measured with respect to the mica substrate (Fig. 7). This agrees with previous reports on $TiSe_2$ monolayers synthesized by epitaxial growth and also corresponds to the separation between $TiSe_2$ layers in the three-dimensional lattice (c~0.60 nm) [2].

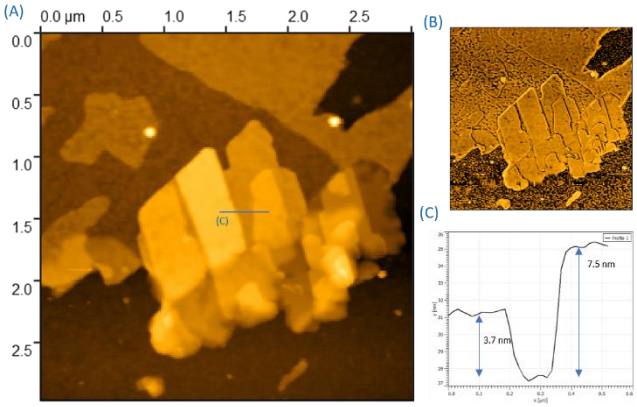


**Fig. 6.** (A) 3x3 µm topography image of $Cu_xTiSe_2$ (x=0) sheets obtained with AFM in AC mode. An agglomeration of two-dimensional $TiSe_2$ sheets with different heights is observed. (B) Phase image. $TiSe_2$ sheets can be distinguished from the substrate (mica) due different mechanic proprieties. (C) The height profile marked in figure (A) is graphed from right to left. Two steps of 3.7 and 7.4 nanometers between sheets are measured, which corresponds to the height of six and twelve $TiSe_2$ monolayers (~0.60 nm) respectively.

The size distribution of the sheets is really difficult to evaluate due to limitations of the microscope's maximum scanning field (10x10 µm), since in general their lateral dimensions are greater than 10 microns. On the other hand, the observations through an optic microscope allows to see the large sheets, but not the small ones.

It can also be seen in Fig. 7 that the sheets have small defects (holes). This is most likely due to defects on the original crystal.

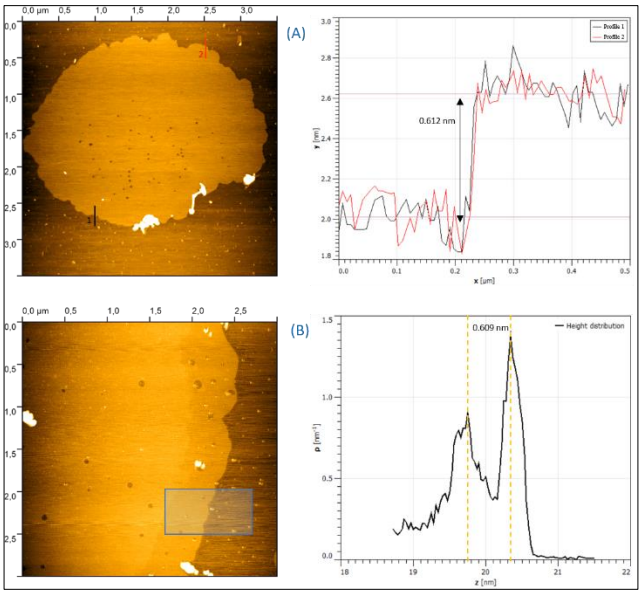


**Fig. 7.** Topographic images of $TiSe_2$ sheets with a size of 3.5x3.5 and 3x3 micrometers, obtained with AFM in acoustic mode. $TiSe_2$ monolayers are observed with heights of around 0.60 nm in both images. In (A), the topography is measured directly using two height profiles. In (B), the distance between the sheet and the mica substrate is obtained by means of a height distribution.

## 4. Conclusions

From the images obtained by AFM, it is concluded that unique 2D sheets of $TiSe_2$ can be synthesized and isolated from a solvothermal process using hydrazine as solvent. Applying this method to different $TiSe_2$ crystals it can be concluded that the quality of the exfoliated sheets (extension and thickness) depends not only on the exfoliation process but also on the precursor crystal. Evidently, the presence of copper as a dopant reduces the interaction between sheets and facilitates the exfoliation process. When exfoliating the $Cu_{0.11}TiSe_2$ crystal, a large number of NPs are dispersed in the medium, which makes it difficult to isolate the monolayers. By applying the same process on a $TiSe_2$ pure crystal, sheets of a few monolayer thick are obtained, while when working on a crystal with a slightly lower purity, the exfoliation of the material is achieved and the monolayers can be isolated. These sheets have some defects (holes) resulting from defects in the precursor crystal.

The exfoliation process is a one-step process and very easy to implement. This method allows to obtain $TiSe_2$ monolayers in larger volumes than by epitaxial growth, although it does not guarantee the same quality in the sheets.


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