Monodisperse size-controlled 1T'-WS$_2$ nano-monolayers with high colloidal stability

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ABSTRACT: The difference between in-plane and out-of-plane bonding energy of transition metal dichalcogenides has provided the possibility of isolating single layers. A one step synthesis protocol to produce size-controlled single layers has always been challenging. Here we developed a new colloidal synthesis to produce monodisperse size-controlled 1T'-WS$_2$ nano-monolayers with outstanding colloidal stability by using 1-octadecanethiol as the coordinating agent. Changes in the reaction time and amount of coordinating agent regulate the mean size of the nanosheets. We investigated the effect of octadecanethiol and injection rate on the dispersion and mean-size, using UV-Vis spectroscopy, X-ray diffraction techniques, and transmission electron microscopy. Furthermore, thermogravimetric analysis and Fourier transform infrared spectroscopy allow for ligands detection and analysis at the surface of the nanosheets. These results open a new pathway to synthesize, control and explore the properties of nanoscale transition metal dichalcogenides.

Introduction

Transition metal dichalcogenides (TMDCs) are lamellar materials with strong covalent in-plane bonding and weak van der Waals inter-layer interaction, classifying them as van der Waals solids.$^{1,2}$ Tunable bandgap, high carrier mobility, and large surface area make these materials relevant for different applications in electronics,$^3$ optoelectronics,$^4$ and catalysis.$^5$ In addition, because they can possess meta-stable crystal structures (octahedral or distorted octahedral), they are candidates for a considerable number of applications, such as hydrogen evolution reaction (HER) and electrode materials for sodium ion batteries.$^6$–$^8$

As a consequence of different bonding energies (strong in-plane and weak inter-layer bonding), isolation of single monolayers is achievable, which creates a high surface area, induces quantum confinement and bandgap transformation.$^9$ This alluring feature results from a lack of symmetry due to the reduction in the size to a single monolayer.$^{10,11}$ Due to these unique properties and numerous potential applications of TMDCs monolayers, the preparation of single layer materials and control of their size have attracted much attention.$^{12,13}$

Different thin layer preparation techniques have been developed and applied over the years, such as exfoliation techniques,$^{14,15}$ substrate growth techniques,$^{16,17}$ and colloidal synthesis.$^{18}$ But so far, no studies have succeeded in synthesizing size-controlled and well-dispersed nano-monolayers. Colloidal synthesis of TMDCs could be a promising strategy to produce a scalable amount of nanosheets by modifying the experimental parameters.$^{19}$ It has been almost one decade since the first colloidal synthesis of WS$_2$ nanosheets was developed, yet this field suffers from the lack of a direct colloidal protocols to produce both well-dispersed and size controlled WS$_2$ nanosheets. Previous work from our group reported a protocol to produce 1T-WS$_2$ nanosheets, and by a modification, 2H-WS$_2$ nanoflowers were also synthesized.$^{20}$ However, these 1T-WS$_2$ nanosheets were severely defected. Zhou et al. developed another hot injection protocol to synthesize WS$_2$ nanosheets. Although they managed to control the number of layers by reinjection of the precursors, the nanosheets were not well-dispersed.
Yin et al. also developed a colloidal protocol to produce 1T'-WS$_2$ nanosheets by one-pot synthesis. However, TEM and STEM images support the formation of 1T'-WS$_2$ nanochains with 162 nm diameter assembled nanosheets. Son et al. developed a protocol to produce colloidal quantum dots of WS$_2$, where they sonicated WS$_2$ powders in an appropriate solvent, then separated the WS$_2$ quantum dots. More recently, Liu et al. developed a comprehensive colloidal protocol to produce metallic phase nanosheets of MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$. In the last step of the synthesis, they induced phase change by annealing the nanosheets under argon atmosphere at 500°C for 1 hour. TEM images show that the nanosheets are neither monodisperse nor colloidal stable. This last study does not yet fulfill the aforementioned demand for colloidally stable and size-controlled nanosheets of WS$_2$.

This paper presents a novel colloidal protocol to produce well-dispersed and size-controlled nano-monolayers (NMLs) of 1T'-WS$_2$. We develop a colloidal synthesis protocol in which 1-octadecanethiol (ODT) is used as the tungsten coordinating agent, reducing its reactivity and allowing for a better synthetic control. We use different characterization techniques such as UV-Vis spectroscopy, powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), and small angle X-ray scattering (SAXS) to prove that the products of the synthesis are colloidal stable 1T'-WS$_2$ monolayers. Additionally, Fourier transform infrared spectroscopy (FTIR), ligand exchange, and thermogravimetric analysis (TGA) are used to probe the nature of the NMLs surface ligands. Finally, we demonstrate control over the size of 1T'-WS$_2$ NMLs by changing the amount of ODT as well as the reaction time, producing monodisperse NMLs with mean sizes ranging from 10 to 60 nm diameter. This high-yield reaction
leads to the formation of the highest quality nano-monolayers that have been synthesized to date. We believe this new colloidal synthesis can spur the widespread study and use of colloidal TMDC nano-monolayers.

Results and discussion

The previous WS\textsubscript{2} synthetic protocol developed by our group consisted of a slow precursor injection at high temperature, where oleylamine (OAm) was the solvent and a mixture of oleic acid (OA) and OAm were used for the precursors injection.\textsuperscript{20} In this case, OAm is crucial for the reaction as it reacts with the sulfur precursor, CS\textsubscript{2}, during the injection mixture preparation and produces oleylammonium dithiocarbamate, which in turn decomposes at high temperature to oleylammonium sulfide. OA coordinates partially with tungsten hexachloride and regulates the reactivity of this tungsten source. But at high temperatures (depending on the environment, between 200°C to 350°C) OA can decompose or react with oleylamine, yielding water or hydroxides which can induce oxidation of the nanosheets.\textsuperscript{25} Hence, to eliminate this partial oxidation of tungsten disulfide, OA should be suppressed from the reaction. In a preliminary experiment, OA is totally suppressed from the protocol and WCl\textsubscript{6} is dissolved directly in OAm in the injection mixture. The other synthetic parameters remained the same, with slow injection (30 min) of the precursor mixture at high temperature in OAm.

After synthesis, UV-Vis absorption spectroscopy of a diluted sample (Figure 1a) shows an excitonic feature at 612 nm, which is characteristic of the 2H structure and a strong deep red and infrared absorption coming from the presence of 1T' domains.\textsuperscript{26} This first characterization already indicates the presence of both phases in the product: 2H and 1T' WS\textsubscript{2}.

PXRD measurement (Figure 1b) performed on a drop-casted sample on a low background silicon sample holder confirms the existence of the two phases. Although oscillations in the low angles can be due to a variety of
reasons, they can be a characteristic of stacking of lamellar materials. However, in this case, as the distances between the peaks are not the same, they are not only simple stacks of monolayers. The peak at 14° corresponds to the 2H (002) plane reflection, and confirms the formation of 2H-WS₂ multilayers. In the inset, the area between 30° and 40° is magnified to better illustrate the presence of the 1T’ and 2H phases. The peak at 31.8° corresponds to the reflection from (2-20) of 1T’-WS₂ and the peak at 32.8° corresponds to the reflection from (100) of 2H-WS₂. This confirms that the WS₂ nanosheets synthesized using this pure OAm protocol are a mixture of 1T’ and 2H-WS₂.²⁰

In contrast with the previous study, where the 2H-WS₂ formed as aggregated nanoflowers, TEM observation shows that this polymorphic WS₂ is formed as nanosheet multilayers (Figure 1c,d), with a mean diameter of (82 ± 12) nm. The diversity of contrast between different nanosheets confirms that nanosheets are of different thicknesses, partially aggregated or formed of multilayers. Furthermore, the size dispersion of the produced nanosheets is large (see Figure 3a).

In the original protocol, OA has been used to form a tungsten oleate complex that regulate the reactivity of the tungsten precursor. This preliminary experiment highlights the strong dependence of this WS₂ colloidal synthesis on the precursor activity. Strong activity leads to aggregated 2H-WS₂ whereas lower precursors activity can lead to 1T’-WS₂ monolayers or polymorphic samples if the activity is not low enough. As a conclusion, an oxygen-free coordinating agent is needed to coordinate further with tungsten hexachloride and regulate the reactivity of the tungsten precursor to improve the dispersion and produce pure 1T’ monolayers.

Thiols or thiolates can play several different roles in the 1T’-WS₂ NML synthesis. They can either act as strong complexing agents for tungsten, thereby tuning its reactivity, or they can be an additional sulfur source, as previously discussed in the literature.²⁷ Additionally, they can act as the main ligands stabilizing the NMLs in solution. In the injection mixture, oleylamine reacts with carbon disulfide at room temperature and produces oleylammonium dithiocarbamate, which decomposes at high temperature to oleylammonium sulfide (when injected into the reaction mixture). Tungsten hexachloride reacts with thiols in the reaction mixture and forms tungsten thiolate. The tungsten thiolate react in turn with oleylammonium sulfides to ultimately generate 1T’-WS₂.²⁰ At this point, tungsten thiolate can also thermally decompose into WS₂. These hypotheses are tested in the following where a new protocol is developed using alkanethiols as the coordinating agents (detailed under Methods).
The UV-Vis spectra of WS$_2$ NMLs synthesized using different alkanethiols (dodecanethiol DDT, hexadecanethiol HDT, and octadecanethiol ODT) (Figure 2a) are characteristic of the pure metallic 1T' phase, as there is high absorption in the entire spectrum and no excitonic features. Comparing the absorption spectra with other studies supports the formation of pure 1T' phase. X-ray diffractograms (Figure S2) further confirm that all the syntheses using alkanethiols yield phase-pure 1T’ WS$_2$ nanosheets (evidenced by the absence of 2H peaks, and especially at 32.8°).

Figure 2b displays TEM images of the well-dispersed WS$_2$ NMLs obtained using dodecanethiol (DDT). The homogenous contrast of different nanosheets supports that they are well-dispersed NMLs. However, Figure S1a shows that regions exhibiting minor aggregation exist. Thiols with longer chains, specifically hexadecanethiol (HDT) and octadecanethiol (ODT), are also explored to investigate the effect of thiols on the nanosheets synthesis and dispersion. TEM images (Figures 2c, d) demonstrate that increasing the chain length of the alkanethiol decreases the mean-size of the NMLs and improves the dispersion. However, Figures S1b, c show that the nanosheets synthesized by HDT are partially aggregated, whereas the use of ODT as the coordinating agent leads to the formation of well-dispersed nanomonolayers. Using thiols as the coordinating agent improves both the colloidal stability and the size dispersion. Figures 3b-d show the monodisperse size dispersion of the WS$_2$ NMLs synthesized by different thiols.

Since these thiols-synthesized NMLs are well-dispersed, we initially hypothesized that thiolates are attached to the surface of NMLs. Due to steric hindrance imparted by the long alkyl chain, the dispersion may then be improved. This is consistent with the colloidal stability enhancement induced by increasing the length of the thiol. However, in the following sections we will show that the surface is not passivated by thiols, and in fact OAm acts as the sole surface ligand present.
PXRD has been performed on a drop-casted sample on a low background silicon sample holder. Figure 4a

Figure 4: a) PXRD diffractograms of rT'-WS₂ synthesized by different thiols as the coordinating agent. b) SAXS diffractograms of well-dispersed, semi-aggregated, and aggregated rT'-WS₂ NMLs obtained with ODT. c) HAADF-HRSTEM picture of ODT rT'-WS₂ NMLs.
represents the PXRD diffractograms of 1T'-WS$_2$ NMLs with the three different thiols used in the synthesis. PXRD can be a good method to measure the distance between layers in NMLs when they orient flat on the substrate during sample deposition and drying. The series of low-angle oscillations are characteristic of the interlayer distance of stacks of 2D materials and are observable for all three of the 1T'-WS$_2$ NMLs synthesized with thiols, with remarkable coincidence in the oscillation peaks. The position of the smallest measured angle for all of the NMLs is at 7°, which corresponds to the reflection from the second oscillation, as the spacing between peaks is 3.5° (Figure 4a). The position of the peaks implies a distance between NMLs of 2.7 nm, which is in good agreement with the distance between nanosheets previously reported, which was measured by STEM imaging. Small angle x-ray scattering (SAXS) was also performed on the well-dispersed WS$_2$ NMLs obtained with the ODT protocol, confirming both the absence of aggregation in toluene, and illustrating their high colloidal stability. For comparison purposes, aggregation has also been induced by controlled addition of ethanol at different volumetric fractions. On slightly aggregated and aggregated NMLs (Figure 4b), SAXS measurements confirm that the thickness of 1T'-WS$_2$ NMLs with an organic ligand layer is about 2.7 nm. It should be stressed that this value is independent of the thiol used during the synthesis (Figure S3), suggesting that thiols are not the main stabilizing ligands here. Considering the thickness of the crystalline portion of a single monolayer which is reported as 0.6 nm, about 2 nm originates from the double ligand layer. This is much smaller (almost two times) than twice an OAm molecule, which shows that there is a strong interdigitating of the alkyl chains. Figure S4 displays a photograph of colloidal dispersions of WS$_2$ NMLs synthesized using the three thiols (DDT, HDT, and ODT) one month after synthesis. It confirms that the WS$_2$ NMLs synthesized using the procedure with thiols are colloidally stable for an extended period of time.

Although these thiols have different chain lengths (from 12 carbons in the backbone for DDT to 18 carbons for ODT), the inter-layer distance stays the same. These results are in stark contrast with the assumption that the improvement in the dispersion is caused by the presence of thiols on the surface. From this observation, two possible conclusions can be drawn: either the surface is exclusively passivated by OAm, or there is a mixture of OAm and thiols. In both cases, the inter-layer distance would be dictated by the presence of OAm, and thus the following characterizations have been performed to exclude the presence of any residual thiols.

To check the presence of such residual thiols on the surface of the nanosheets, we first performed FTIR on dried nanosheets to eliminate solvent effects. The FTIR spectra of different compounds is shown in Figure S5. Increasing the chain length in the thiols induces a shift in the S-H bonding, which causes the S-H bonding peak for ODT to occur below 600 cm$^{-1}$. It is no longer measurable using our setup. Furthermore, WS$_2$ NMLs absorb a high amount of FTIR signals, and less than 20% of the infrared light is collected after interaction with the sample. Consequently, the signal-to-noise ratio is low and the results are difficult to interpret. For these reasons, FTIR results were inconclusive for analyzing the ligands composition on the WS$_2$ NMLs synthesized with thiols, and the results can neither prove nor disprove the presence of thiols on the NMLs surface.

Thermogravimetric analysis has been performed on completely dried NMLs in an attempt to determine both the ligand identity and the ligand density on the WS$_2$ surface. This is made possible by the unique decomposition temperature for each different thiol and for OAm (Figures 5 and S7). After synthesis, the final product is a mixture of WS$_2$ nanosheets with ligands on their surface. In good accordance with PXRD results, TGA shows that WS$_2$ synthesized using different thiols and from pure OAm have the same ligands decomposition temperature onset. The first derivative of the TGA curves determines the temperature at which the greatest rate of change in the weight loss happens. Figure 5b shows these curves for WS$_2$ nanosheets synthesized by ODT as the coordination agent, and for WS$_2$ nanosheets synthesized using the pure OAm synthesis. This confirms that both samples have the same ligands on the surface, as both peaks are located at the same temperature (312°C).

Furthermore, removing the ligands by thermal decomposition allows for determination of the net weight of the nanosheets. Heating the nanosheets above 400°C leads to complete decomposition of the ligands on the surface,
with the experiment being performed under nitrogen flow to avoid oxidation of the NMLs themselves. TGA curves of different syntheses show different reductions in mass, meaning the different samples have different amounts of ligands on the surface. These results indicate that the surface ligands account for 20%, 18%, 15%, and 17% of the initial mass for WS$_2$-ODT, WS$_2$-HDT, WS$_2$-DDT, and WS$_2$-OAm, respectively (Figure S8). The reduction in the number of ligands at the surface of the nanosheets leads to partial instability of the nanosheets. In the case of WS$_2$-OAm, the instability can additionally come from the presence of 2H domains in the nanosheets inducing the multilayer structure.

The reaction stoichiometry indicates a large excess of sulfur, making tungsten the limiting reagent. Therefore, by measuring the mass of the NMLs before and after TGA analysis and comparing it with the completed reaction calculated based on the amount of reactants, both the yield of reaction and the number of ligands on the surface are quantifiable. Calculations indicate that thiols not only improve the dispersion, but also improve the yield of the reaction, as indicated by the increase in yield from 73% for pure oleylamine synthesis to 84% for 1T'-WS$_2$ with DDT, 86% for 1T'-WS$_2$ with HDT, and 90% for 1T'-WS$_2$ with ODT.

The onset of decomposition temperatures of tungsten thiolates can also be indicative of their stability in solution during synthesis, with a lower onset temperature correlating to lower stability. This has been investigated as well using TGA, showing an onset of decomposition temperature for W(DDTate)$_6$ at 223°C, W(HDTate)$_6$ at 249°C, and W(ODTate)$_6$ at 268°C (Figure S7). The increase in the decomposition temperature occurs with increasing chain length of the thiol. An attractive hypothesis is that the in-situ formation of tungsten thiolate leads to the creation of well-dispersed 1T'-WS$_2$ NMLs by regulating the reactivity of the tungsten precursor. Reducing the reaction rate by conjugating the reactants produces the metastable 1T' phase. This phase generally occurs due to the presence of excess charges in the NMLs and then in the reaction system. Thus, due to the presence of charges on the nanosheets, oleylammonium ligands are bound to the surface and are responsible for the colloidal stability.

Another protocol was developed to clarify the role of thiols in the reaction. As has been already discussed, the reaction of WCl$_6$ with thiols forms tungsten hexathiolate and HCl. This reaction happens at room temperature, so instead of adding ODT into the reaction mixture, WCl$_6$, ODT, OAm, and CS$_2$ were mixed to prepare the injection mixture. As explained in detail in the methods section, the injection mixture was added into the OAm at 320°C over a period of 30 minutes. The TEM image and the absorption spectrum are presented in Figure S9. The TEM image illustrates that aggregated nanosheets are produced by this protocol and the absorption spectrum confirms
the formation of the 1T'-WS₂ phase. Although the amount of ODT in both protocols is the same, the dispersion is here completely different. One can hypothesize that when ODT is present in the reaction medium, at every moment during the injection, tungsten precursors are at low concentrations and in presence of a large excess of ODT, which can efficiently bind the tungsten and regulate the reactivity. On the contrary, when ODT is added into the injection mixture, the amount of ODT relative to the reactive tungsten species during injection increases over time in the injection mixture and is too low at the early stages of the synthesis to properly regulate the NMLs growth.

Since a direct measurement through FTIR was inconclusive, additional experiment have been conducted to assess if the surface ligands are exclusively OAm. As such, a ligand exchange has been performed on the NMLs synthesized by ODT as the coordinating agent to verify if the mean distance between NMLs changes. As described in further detail under Methods, octylamine has been used for this exchange. Figure S10 illustrates the PXRD diffractograms of 1T'-WS₂ NMLs before and after ligand exchange. The shift in the low angle oscillations supports that the interplanar distance has decreased. Calculating the distance of NMLs after ligand exchange shows that the spacing has decreased from 2.7 nm to 2.07 nm. This variation is induced by the shorter size of octylamine (8 carbons in the chain) compared to OAm (with 18 carbons and an unsaturation). These results further support that there is no ODT on the surface of NMLs, as the ligand exchange induced a change in the interplanar distance.

Clarifying the role of ODT in the synthesis of colloidally stable NMLs paves the way to develop protocols to synthesize size-controlled NMLs. There are different key factors in wet chemistry synthesis that can modify the final nanocrystal size and morphology. Because the 1T'-WS₂ NMLs synthesized by ODT are colloidally stable nanosheets, different parameters in this protocol are modified to produce size-controlled and well-dispersed NMLs with diameters ranging from 10 to 60 nm. If the formation mechanism of WS₂ NMLs occurs through nucleation and growth, regulating the injection rate should alter the rate of nucleation, and the mean size and the size-dispersion of the nanosheets should also change. Thus, the first parameter used to control the mean size of the final products is the injection rate. Reducing injection time should cause an increase in the nucleation rate, and consequently, the mean size should reduce. On the other hand, prolonging the injection time reduces the

Figure 6: TEM image of well-dispersed 1T'-WS₂ NMLs with different mean sizes. Decreasing the amount of coordinating agent (ODT) as well as prolonging the injection time increases the mean size.
concentration of precursors in the reaction mixture, which decreases the nucleation rate, and thus the mean size should increase. Although the jellification of the injection mixture (through oleylammonium dithiocarbamate formation) limits the injection time, diluting the injection mixture with excess OAm (10 mL instead of 5 mL) makes it possible to prolong the injection time.

The other modified factor is the amount of ODT in the reaction mixture. Although it is now quite clear that the dispersion does not improve due to the presence of ODT on the surface of the nanosheets, thiols nature and concentration adjust the reactivity of the tungsten precursor. Thus changing the amount of ODT in the reaction mixture shifts the mean size of the products. New colloidal protocols are then developed to synthesize colloidal stable and size-controlled 1T'-WS₂ NMLs by controlling both the tungsten precursor reactivity with the amount of ODT and the nucleation rate by varying the injection time. TEM images of 1T'-WS₂ nanosheets synthesized with these different protocols are shown in Figure 6. Decreasing the amount of ODT and increasing the injection time causes the NMLs to become larger. Figure S1 present the absorption spectra of 1T'-WS₂ NMLs with different sizes, which confirms the different sized NMLs are all semi-metallic polymorphs. A reduction in the amount of ODT decreases in the stability of the tungsten precursor that in turn increases the NMLs size. Furthermore, for this nucleation and growth mechanism, increasing the injection time dilute the reactant species at any time in the mixture, which decreases the nucleation rate and boosts the growth. Depending on the desired size of NMLs, the injection rate and amount of ODT can then be varied to finely control it.

Conclusions

In conclusion, a new protocol has been developed to produce colloidal stable, monodisperse and size-controlled 1T'-WS₂ NMLs with nearly 90% chemical reaction yield. Three different alkanethiols were used as the tungsten coordinating agents, improving the colloidal stability and yield of the reaction by regulating the reactivity of the tungsten precursor. UV-Vis absorption spectroscopy and PXRD confirm that the NMLs produced are 1T'-WS₂ and TEM images and SAXS support that the NMLs are well dispersed. A combination of PXRD, TGA, and ligand exchange supports that the surface chemistry is not changed, regardless of the thiol used, and implies that the NMLs are systematically stabilized with oleylamine/oleylammonium ligands. 1T'-WS₂ NMLs with different mean sizes (10-60 nm) are then synthesized by changing the amount of thiol and reaction time to regulate the nucleation rate and the tungsten precursor reactivity. This new protocol yields the most stable WS₂ monolayers that have been colloidally synthesized to date. We strongly believe this new colloidal protocol paves the way for other studies into the applications of 1T and 2H-WS₂, such as electrocatalysis, sensors, and optoelectronic devices. This protocol could also potentially be extended to other group VI TMDCs to produce well-dispersed and size-controlled NMLs of all the members of this family.

Methods

Materials:

1-octadecanethiol (ODT) (97%, Sigma-Aldrich), hexadecanethiol (HDT) (95%, Sigma-Aldrich), dodecanethiol (DDT) (98%, Sigma-Aldrich), oleylamine (OAm) (80%-90%, Acros), tungsten hexachloride (WCl₆) (99.9%, Acros), carbon disulfide (CS₂) (99%, Sigma-Aldrich), hexane (95%, Carlo erba), anhydrous ethanol (99.9%, Carlo erba), toluene (98%, VWR-BDH chemicals), acetonitrile (99.9% Sigma-Aldrich), and 1-octylamine (99% Alfa Aesar) were used as received with no additional purification.

Synthesis of WS₂ nanosheets without thiols:

In a typical synthesis, 15 mL (46.6 mmol) OAm was added into a 50 mL three-neck-flask and degassed under vacuum at 80°C for 1 hour. Then the reaction mixture was heated to 320°C under an argon atmosphere. 50 mg (0.126 mmol) WCl₆ was dispersed in 5 mL (15.5 mmol) OAm and just before the injection, to avoid jellification, 240 µL CS₂ was added to the mixture. The injection mixture was added dropwise to the reaction mixture over the course of 30 minutes. After injection, the reaction mixture was cooled down to room temperature and the
product was centrifuged and washed 3 times with a mixture of hexane and ethanol. The product was dispersed in 10 mL toluene for storage.

**Synthesis of WS$_2$ nano-monolayers:**

In a typical synthesis, 35 mmol thiol (10 gr ODT, 9 gr HDT, or 7 gr DDT) was dissolved in 15 mL (46.6 mmol) OAm. The mixture was added into a 50 mL three-neck-flask and degassed under vacuum at 80°C for 1 hour. Then, the reaction mixture was heated to 320°C under an argon atmosphere. 50 mg (0.126 mmol) WCl$_6$ was dispersed in 5 mL (15.5 mmol) OAm and just before the injection, to avoid jellification, 240 µL CS$_2$ was added to the mixture. The injection mixture was added dropwise to the reaction mixture over the course of 30 minutes. After injection, the reaction mixture was cooled to room temperature and the product was centrifuged and washed 3 times with a mixture of hexane and ethanol. The product was dispersed in 10 mL toluene for storage.

**Synthesis of tungsten thiolates:**

In a 20 mL vial under a fume hood, 50 mg (0.126 mmol) WCl$_6$ was mixed in 0.756 mmol thiol (216 mg ODT, 195 mg HDT, 151 mg DDT), 5 mL absolute ethanol was added to the mixture to insure thorough mixing. As the reactants were mixed, bubbles formed and the color of the mixture turned dark red. When the mixture stopped bubbling, the product was centrifuged and washed 3 times with a mixture of hexane and acetonitrile. The resulting products were silvery-white solid particles.

**Synthesis of different size WS$_2$ nano-monolayers:**

$D_{\text{mean}} = 14$ nm:

In a typical synthesis, 10 gr ODT (35 mmol) was dissolved in 15 mL (46.6 mmol) OAm. The mixture was added into a 50 mL three-neck-flask flask and degassed under vacuum at 80°C for 1 hour. Then, the reaction mixture was heated to 320°C under an argon atmosphere. 50 mg (0.126 mmol) WCl$_6$ was dispersed in 5 mL (15.5 mmol) OAm and just before the injection, to avoid jellification, 240 µL CS$_2$ was added to the mixture. The injection mixture was added dropwise to the reaction mixture over the course of 15 minutes. After injection, the reaction mixture was cooled to room temperature and the product was centrifuged and washed 3 times with a mixture of hexane and ethanol. The product was dispersed in 10 mL toluene for storage.

$D_{\text{mean}} = 38$ nm:

In a typical synthesis, 5 gr ODT (17.5 mmol) was dissolved in 15 mL (46.6 mmol) OAm. The mixture was added into a 50 mL three-neck-flask and degassed under vacuum at 80°C for 1 hour. Then, the reaction mixture was heated to 320°C under an argon atmosphere. 50 mg (0.126 mmol) WCl$_6$ was dispersed in 10 mL (31 mmol) OAm and just before the injection, to avoid jellification, 240 µL CS$_2$ was added to the mixture. The injection mixture was added dropwise to the reaction mixture over the course of 60 minutes. After injection, the reaction mixture was cooled to room temperature and the product was centrifuged and washed 3 times with a mixture of hexane and ethanol. The product was dispersed in 10 mL toluene for storage.

$D_{\text{mean}} = 45$ nm:

In a typical synthesis, 5 gr ODT (17.5 mmol) was dissolved in 15 mL (46.6 mmol) OAm. The mixture was added into a 50 mL three-neck-flask and degassed under vacuum at 80°C for 1 hour. Then, the reaction mixture was heated to 320°C under an argon atmosphere. 50 mg (0.126 mmol) WCl$_6$ was dispersed in 10 mL (31 mmol) OAm and just before the injection, to avoid jellification, 240 µL CS$_2$ was added to the mixture. The injection mixture was added dropwise to the reaction mixture over the course of 120 minutes. After injection, the reaction mixture was cooled to room temperature and the product was centrifuged and washed 3 times with a mixture of hexane and ethanol. The product was dispersed in 10 mL toluene for storage.

$D_{\text{mean}} = 59$ nm:
In a typical synthesis, 5 gr ODT (17.5 mmol) was dissolved in 15 mL (46.6 mmol) OAm. The mixture was added into a 50 mL three-neck-flask and degassed under vacuum at 80°C for 1 hour. Then, the reaction mixture was heated to 320°C under an argon atmosphere. 50 mg (0.126 mmol) WCl₆ was dispersed in 10 mL (31 mmol) OAm and just before the injection, to avoid jellification, 240 µL CS₂ was added to the mixture. The injection mixture was added dropwise to the reaction mixture over the course of 180 minutes. After injection, the reaction mixture was cooled to room temperature and the product was centrifuged and washed 3 times with a mixture of hexane and ethanol. The product was dispersed in 10 mL toluene for storage.

**WS₂ nanosheets synthesis with injection of thiols:**

15 mL (46.6 mmol) OAm was degassed at 80°C for 1 hour in a three-neck-flask and then heated to 320°C. 50 mg (0.126 mmol) WCl₆ was dispersed in a mixture of 5 mL (15.5 mmol) OAm and 5 gr (17.5 mmol) ODT. Just before the injection, 240 µL CS₂ was added to the mixture and the injection mixture was injected dropwise over the course of 1 hour. After injection, the reaction mixture was cooled to room temperature and the product was centrifuged and washed 3 times with a mixture of hexane and ethanol. The product was dispersed in 10 mL toluene for storage.

**Ligand exchange:**

200 µL (2 mmol) octylamine was added to 500 µL synthesized WS₂ dispersed in 500 µL toluene in a closed vial. The mixture was kept in the oven at 65°C. After 24h, the samples were centrifuged and washed 3 times with ethanol. Nanosheets were dispersed in 10 µL ethanol for PXRD characterization.

**Characterization methods:**

**TEM:** Transmission electron microscopy (TEM) images were acquired on a JEOL JEM-2100 TEM equipped with a LaB₆ electron source, operating at 200 kV. Samples were prepared by drop-casting a diluted sample on a 400-mesh copper grid.

**UV-Vis spectroscopy:** The UV-Visible absorption spectra of 15 µL of WS₂ nanosheets diluted in 3 mL toluene were recorded using an AVANTES Avaspec ULs2048L spectrometer.

**PXRD:** Powder X-Ray Diffraction (PXRD) diffractograms were recorded on a PANalytical PIXcel1D Medipix3 detector with a copper tube operating at 30 kV. All the samples were prepared by drying few a drops of the WS₂ dispersed in ethanol on a low background silicon sample holder.

**TGA:** Thermogravimetric analysis (TGA) measurements were performed on a Netzsch STA 409 PC Luxx thermogravimetric analyzer. Nanomonolayer samples were dried to a powder and portions of (10 ± 2) mg were loaded in an Al₂O₃ crucible. Tungsten thiolates were dried similarly before being diluted to an approximate concentration of 10% in a matrix of powdered alumina. Samples were heated from 25 °C to 550 °C at a rate of 10.0 °C/min under flow of nitrogen gas.

**FTIR:** Fourier-transform infrared spectroscopy (FTIR) measurements were performed on an IR Affinity-1 Shimizu FII spectrophotometer with MIRacle natural diamond ATR – PIKE. Different samples were drop-casted directly onto the crystal optic. Concentrated solutions of WS₂ nanomonolayers were dried on top of the crystal optic. The range of measurement was 600-4000 wavenumber (cm⁻¹) and the acquisition time for each sample was 300 s.

**SAXS:** Small-angle X-ray scattering (SAXS) measurements were carried out on a XENOCS Xeuss 3.0 instrument using a fixed tension of 50 kV, a current of 0.6 mA, and a sample-to-detector distance of 0.28 m. The typical accessible range of scattering vector modulus q was 0.01 to 1 Å⁻¹, for q=(4π/λ) sin(θ), where 2θ is the scattering angle and λ = 1.54 Å is the wavelength. The intensity was radially averaged to yield intensity versus q data. Typical exposure times were 300 seconds, repeated for 5 scans before being averaged and background-corrected with the corresponding solvent blank. For aggregated samples, colloidal dispersions were destabilized using varying amounts of ethanol (10%v/v, 20%v/v or 50%v/v), and loaded into glass capillaries.
ASSOCIATED CONTENT

Supporting Information. Supporting Information containing TEM images, PXRD patterns, SAXS diffractograms, FTIR spectra, TGA curves, and absorption spectra. “This material is available free of charge via the Internet at http://pubs.acs.org.”

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ABBREVIATIONS

NML, nano-monolayer; OAm, oleylamine; OA, oleic acid; ODT, octadecanethiol; HDT, hexadecanethiol; DDT, dodecanethiol; TEM, transmission electron microscopy; PXRD, powder X-Ray Diffraction; TGA, thermogravimetric analysis; FTIR, fourier-transform infrared; SAXS, small angle X-ray scattering.

REFERENCES


