Short Pulse Laser Synthesis of Transition-Metal Dichalcogenide Nanostructures under Ambient Conditions

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ABSTRACT: The study of inorganic nanometer-scale materials with hollow closed-cage structures, such as inorganic fullerene-like (IF) nanostructures and inorganic nanotubes (INTs), is a rapidly growing field. Numerous kinds of IF nanostructures and INTs were synthesized for a variety of applications, particularly for lubrication, functional coatings, and reinforcement of polymer matrices. To date, such nanostructures have been synthesized mostly by heating a transition metal or oxide thereof in the presence of precursor gases, which are however toxic and hazardous. In this context, one frontier of research in this field is the development of new avenues for the green synthesis of IF structures and INTs, directly from the bulk of layered compounds. In the present work, we demonstrate a simple room-temperature and environmentally friendly approach for the synthesis of IF nanostructures and INTs via ultrashort-pulse laser ablation of a mixture of transition-metal dichalcogenides in bulk form mixed with Pb/PbO, in ambient air. The method can be considered as a synergy of photothermally and photochemically induced chemical transformations. The ultrafast-laser-induced excitation of the material, complemented with the formation of extended hot annealing regions in the presence of the metal catalyst, facilitates the formation of different nanostructures. Being fast, easy, and material-independent, our method offers new opportunities for the synthesis of IF nanostructures and INTs from different bulk metal chalcogenide compounds. On the basis of the capabilities of laser technology as well, this method could advantageously be further developed into a versatile tool for the simultaneous growth and patterning of such nanostructures in preselected positions for a variety of applications.

INTRODUCTION

Since the discovery of the nested inorganic fullerene-like nanoparticles (IF-NPs) and inorganic nanotubes (INTs) of tungsten disulfide (WS2) and molybdenum disulfide (MoS2),† by heating thin metal films of W and Mo in the presence of gaseous H2S, a whole new field opened up with opportunities in research and applications. The multilayered two-dimensional elements are unstable in their microscopic form and spontaneously form closed structures with a hollow core. Layered materials formed from inorganic elements are abundant. In bulk form, these structures appear as platelets, wherein each platelet is composed of molecular slabs held by weak van der Waals forces. Typical examples of such structures from WS2 and MoS2 were reported in numerous works. Transition-metal dichalcogenides (TMDs) are trilayer X−M−X sandwiches, where X = S or Se and M = a transition metal. Besides these, numerous fullerene-like NPs and INTs were synthesized through the years from different layered structure materials, including BN,‡ TaS2,§ and NiCl2,∥ and ternary layered (misfit) compounds.5 Owing to their remarkable properties, many studies have focused on the stability and the structure6 of the IF-NPs and INTs of WS2 and MoS2 in addition to their significant mechanical, optical, and electronic properties.7 As a result, IF nanostructures from WS2 and MoS2 have been effectively used and commercialized in various applications, particularly as solid lubricants.8 In addition, numerous applications of these NPs have been proposed, including in reinforcing polymer nanocomposites,9 nanoelectronics,10 energy production,11 and storage.12 Besides this, the nontoxic nature of such materials, as has been pointed out in several studies,13 is a prime motivation for medical applications.14 The growth mechanism of these structures has become a highly explored topic for many researchers.15 One can distinguish between two main research strategies: (a) high-temperature synthesis under a chemically controlled atmosphere and (b) using energy burst to ablate powder and induce a reaction under far from equilibrium conditions. The studies on (a) were mostly based on the reactions of hydrogen and hydrogen sulfide or sulfur-containing vapors with metal-oxide NPs or another metal precursor at typical temperatures between 500 and 1000 °C. These conditions allow for the synthesis of metastable phases of MX2 under not far from equilibrium conditions. The most common synthesis method for large-scale production of IF-NPs and INTs is sulfidization of metal oxides under reducing conditions.16 Here, the reaction parameters can be modified and controlled.

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systematically, enabling the mass production of the IF-NPs and INTs of WS\textsubscript{2} as well as MoS\textsubscript{2} for a variety of applications. On the other hand, reactions in the (b) category occur under far from equilibrium conditions and cannot be easily controlled. Despite the great success with the production of single-wall carbon nanotubes and C\textsubscript{60} these methods have not been well developed for their inorganic analogues so far. Fortunately, this kind of reaction opens windows of metastability not accessible for the thermally induced reactions of (a). An excellent proof of concept was the first synthesis of MoS\textsubscript{2} nano-octahedra, which were dubbed the “true inorganic fullerenes”\textsuperscript{17}. In this context, different approaches were used by several research groups, such as arc discharge,\textsuperscript{18} shock waves,\textsuperscript{19} solar ablation,\textsuperscript{17} and laser ablation,\textsuperscript{6b,20} which yielded remarkable results. Another interesting approach was presented recently\textsuperscript{21} utilizing a focused solar beam and a growth promoter in the form of a heavy metal. The beam is generating continuous extreme temperatures exceeding 2500 °C and temperature gradients (10\textsuperscript{3} K/mm) in the presence of a metal catalyst (Pb), which lead to the formation of various inorganic nanotubes. The presence of the metal catalyst seems to promote the growth of new hybrid structures with a metal core–semiconductor shell.

Furthermore, although considerable research has been devoted to the large-scale synthesis of IF nanostructures and INTs, less attention has been paid to avoiding the use of toxic and hazardous gases such as H\textsubscript{2}S and H\textsubscript{2}. Hence, the development of a more environmentally friendly synthetic method remains a challenge.

In this context, we demonstrate here a new synthesis path toward fullerene-like NPs and INTs from the bulk, via ultrafast laser ablation in ambient air (Figure 1). Contrary to previous laser ablation approaches\textsuperscript{6b,20} our method does not require inert conditions. The ultrafast-laser-induced excitation and ablation of the irradiated material lead to extreme temperatures and heat gradients, enabling the synthesis of metastable MX\textsubscript{2} phases under far from equilibrium conditions. Accordingly, this method provides the potential for the synthesis of nanostructures that cannot be attained by conventional synthetic routes. This technique is fast and does not require the use of hazardous precursor gases and thus expensive equipment. Not less important is the possibility for, on-demand, simultaneous growth and patterning of nanostructures in preselected locations. Finally, it is a material-independent technique and thus can be further extended for the direct synthesis of other TMD nanostructures.

### RESULTS

Scanning electron microscopy (SEM) images revealed that laser irradiation of MoS\textsubscript{2} gives rise to nanowhiskers and IF-NPs, whereas that of WS\textsubscript{2} yields INTs. For MoS\textsubscript{2} in particular, the irradiating powder comprises MoS\textsubscript{2} platelets (Figure 2a) decorated with nanowhiskers, with no indication of nanotubes. A closer inspection with transmission electron microscopy (TEM) revealed interesting faceted IF-NPs, colocated in the same area with nanowhiskers, with sizes ranging between 80 and 200 nm, as presented in Figure 3a,b. The layered structure of the walls forming such NPs can be clearly resolved in the respective images. The inset of Figure 3c represents the line profile with the measured interlayer distance to be 0.61 nm, which corresponds to the interlayer distance (c/2) of MoS\textsubscript{2}. Whereas some of the IF-NPs produced appear as having a hollow core, others seem to have a darker contrast inside their interior. Nevertheless, the energy-dispersive spectrometry (EDS) measurements performed on single particles consistently gave an almost perfect 1:2 Mo/S ratio, as presented in the inset of Figure 3d. Besides this, the amount of oxygen was negligible, therefore the possibility of a core composed out of oxidized molybdenum or pure molybdenum can be discarded. Furthermore, the undistorted Mo/S ratio points to a MoS\textsubscript{2} core. High-resolution TEM (HRTEM) imaging, as shown in Figure 4a,b, also revealed sharp edges and corners of these NPs with distinct fringes, whereas the internal structure begins exactly where the layers end. This indicates the inside-out growth mechanism, where a small MoS\textsubscript{2} (nano) platelet serves as a template (growth nucleus), which is subsequently sheathed layer by layer upon irradiation. Figures 5 and 6 represent the TEM images of the sharp corner and a faceted edge, respectively, at different tilt angles. The feature in Figure 5 is virtually unaltered as the tilt...
angle changes from $-20$ to $+20^\circ$; this observation confirms that the imaged feature is a sharp corner. On the other hand, Figure 6 shows a faceted edge, which appears as more rounded at negative angles, whereas it changes into sharper edges upon tilting to $+20^\circ$.

On the other hand, SEM imaging of the irradiated WS$_2$ powder revealed that INTs are growing from WS$_2$ platelets (Figure 7a–d). The nanotubes’ dimensions ranged from 20 to 100 nm in width and were approximately 1 $\mu$m in length. It can be observed that the outermost surface of the exposed platelets appears to be completely covered by INTs. The mild sonication procedure used for the preparation of TEM grids detaches the INTs from the platelets, leaving one of the edges open, whereas the other is usually closed. A representative WS$_2$ nanotube is presented in the

Figure 3. TEM analysis of IF-MoS$_2$ NPs: (a) an assembly and (b) a single IF-MoS$_2$ NP. (c, d) Line profile and EDS measurement, respectively, performed on a single particle.

Figure 4. HRTEM analysis of IF-MoS$_2$ NPs: at low (a) and high (b) magnifications.
TEM image of Figure 8a,b. The interlayer spacing, as shown in the inset of Figure 8a, is close to 0.625 nm, which is slightly larger than the distance between the two neighboring layers of WS₂ (c/2 = 0.62 nm). Moreover, it was observed that some of the INTs synthesized exhibited a hollow core, whereas the rest were filled with material. Because the number of layers on both sides of INTs is the same, as shown in Figure 9a,b, it is possible that the core is made through a posteriori filling of the pre-prepared nanotubes. In analogy to the case of the previously discussed IF-MoS₂ NPs, the amount of oxygen found in the laser-synthesized

Figure 5. TEM tilting experiment of an IF-MoS₂ NP, focused on a sharp corner.

Figure 6. TEM tilting experiment of an IF-MoS₂ NP, focused on a faceted edge.
INT-WS₂ was negligible. On the contrary, by EDS analysis, the W/S ratio was found to be approximately 1:1 in all cases, as shown in the inset of Figure 8b. There can be several explanations for this phenomenon. Most likely, because W is much heavier than both Mo and S, the count rate is rather low. Hence, the deviations of the model calculations for the atom %, which are extracted directly from the detector, are larger. Additionally, this analysis takes into account only specific lines (the K line for sulfur and the L line for tungsten). Although these are the predominant ones, including the other lines may change the W/S ratio. On the other hand, the existence of the core may be attributed to its filling with excess sulfur.

**DISCUSSION**

The first question arising from the experimental findings presented here is the role of lead in the synthesis of the inorganic nanostructures. Back in 2012, MX₂ (M = Mo, W; X = S, Se) nanotubes were produced by solar ablation of the respective powder in the presence of lead. In fact, according to the proposed growth mechanism, the originally ablated MX₂ + Pb powder was first converted into MO₃ₓ⁻ nanowhiskers. The lead atoms were incorporated into the MO₃ₓ⁻ lattice, making it more stable and promoting the growth of a nanowhisker. Further irradiation of the nanowhiskers in the presence of the chalcogenide vapor leads to back-conversion of the metal oxide into MX₂ nanotubes. More recently, core−shell nanotubes and fullerene-like structures of Pb@GaS were obtained via solar ablation of the mixed powder. In this work, GaS layers wrapped the Pb nanotemplate conformably, producing such intriguing nanostructures. In contrast to these cases, no lead was found within or in the vicinity of the IF/INT MoS₂/WS₂ nanostructures produced via the laser ablation approach presented here. Therefore, it can be
concluded that the presence of lead may not play any direct significant role in the production of the nanostructures reported here; further experiments are currently in progress to confirm the insignificant role of lead. Nevertheless, no IF/INT nanostructures were produced by laser ablation of Pb-free powder. Therefore, the comprehensive role of Pb in the synthesis is not fully understood at this time and requires further investigation.

Surprisingly, the same reaction conditions yield substantial amounts of hollow closed structures of MoS$_2$ and WS$_2$ but yet with dissimilar morphology. Although the outcome of the ablation of MoS$_2$ powder is fullerene-like NPs with acute corners, multiwall nanotubes are the main product of the WS$_2$ powder ablation. On the one hand, it points out to the robustness of these nanostructures, which have been previously attained using different chemical strategies. The difference between the reaction products of MoS$_2$ and WS$_2$ is possibly a manifestation of the differences in their chemical stability. In the particular case of MoS$_2$, the ablated plume undergoes rapid oxidation under the intense laser flux in air, whereas the resultant oxide is rather volatile. Therefore, the IF-MoS$_2$ NPs have possibly been formed at the pristine surface left behind the ablated material. It should be emphasized here that the intense laser beam excites a large density of electrons, which eventually give rise to excess heat upon transferring of their energy to the lattice via phonons. Additionally, these photoexcited electrons can also provide a reducing local atmosphere on the surface of the ablated sample. Thus, the ablated MoS$_2$ plume, which resides in the close vicinity of the powder surface, is protected against oxidation and can contribute to the buildup of the IF-MoS$_2$ NPs. On the contrary, WS$_2$ is chemically more stable and does not oxidize as easily as MoS$_2$. Therefore, the WS$_2$ ablation plume is likely to be rich in WS$_x$ vapor, which condenses back onto the mother tip of the tube protruding from the powder crystallites’ surface. Experiments are under progress to monitor the evolution of each kind of nanostructure upon variation of the irradiation parameters.

Large amounts of pure WS$_2$ nanotubes’ phases were obtained in the past by reacting WO$_{3-x}$ and H$_2$S at temperatures as high as 800–900 °C. Several growth mechanisms have been proposed; consequently, a distinction was made between type I and II formation processes. In the case of type I, the nanotubes grow spontaneously at a high rate. Conversely, in the type II process, WO$_{3-x}$ nanowhiskers grow first and are subsequently substituted chemically into WS$_2$ nanotubes. This process is rather slow (it takes a fraction of an hour) and is possibly not relevant to the present experimental conditions. While type I tubes are narrow (up to 40 nm), made of up to 10 walls, and are open ended, type II ones exhibit large diameters (50–150 nm), are usually longer (2–20 μm), and usually have closed tips. In the production process presented here, the situation is quite different. The ultrashort pulses are heating the lattice via a photothermal process but at the same time provide the energy to photochemically break the chemical bonds between W and S and ablate the WS$_2$ moieties, which subsequently give back the energy to the environment and condense (Figure 10). This rapid process is analogous to the type I nanotube growth. As expected, no oxide core was identified in the analysis. Furthermore, as shown in Figure 7b, the tubes form a forest protruding perpendicular to the substrate and exhibit quite uniform length. This growth mode indicates an abrupt supply shortage of the plume, possibly via rapid energy loss to the environment, once the nanotubes reach a critical length. Although type I nanotubes are mostly grown under the conditions used, TEM analysis revealed the presence of a fraction of type II nanotubes in the ablated area. A direct comparison of the two types is presented in Figure 9. Indeed, the nanotube shown in Figure 9a is akin to type I (few layers and a large-diameter core), whereas that in Figure 9b is closer in shape to type II (many layers and a narrow core). Furthermore, it was observed that the nanotubes with a large diameter mostly exhibited a closed tip, whereas the narrower ones showed an
open tip. It can be concluded that the highly excited state conditions formed under ultrafast laser excitation and subsequent ablation give rise to growth processes, which are not necessarily relevant to those observed in high-temperature oven-induced reactions. Nonetheless, our finding that WS₂ nanotubes of similar structures can be produced, in similar or even higher yields compared to those in the alternative approaches, under such entirely different conditions is indicative of the robustness of this structural motif.

## CONCLUSIONS

The synthesis of WS₂ and MoS₂ nanostructures through ultrashort-pulse laser irradiation of the bulk material under ambient conditions is demonstrated. It is shown that although this method produces nanotubes in the case of WS₂, irradiation of MoS₂ under identical conditions leads to IF-NPs. The presented method is performed in ambient air and without use of any toxic precursor gases, making it a simple and environmentally friendly approach to obtaining high-quality inorganic nanostructures. Our results suggest that one can use a scanning laser beam for the formation of inorganic nanostructures at any preselected location and on temperature-sensitive plastic substrates, which is destined to numerous applications, including formation of miniaturized electronic devices or tips for electron emission and scanning probe microscopy.

## EXPERIMENTAL PROCEDURES

### Sample Preparation and Laser Ablation

MoS₂ (or WS₂) powder was mixed with Pb powder, as the metal catalyst, in a 1:1 molar ratio (11 g each). Substrates of Al were sonicated in ethanol for 10 min. Using a silver paint, the mixed powder was attached to the Al substrate. Pulsed laser ablation of the sample was performed in ambient air. A second-harmonic Yb:KGW laser (513 nm, pulse duration 170 fs, pulse repetition rate 60 kHz, fluence = 5.3 W/mm²) was used for these experiments. The sample was mounted on a computer-controlled motorized X–Y translation stage. During the irradiation, the sample was scanned in two orthogonal directions (X and Y) in a fully controlled manner across the focused laser beam in several spots for a duration of 1 min each. The estimated number of laser pulses for each irradiation spot is 3.6 × 10⁸. A schematic of the experimental setup is shown in Figure 1.

### Electron Microscopy

The samples were examined by different electron microscopy techniques. SEM (JEOL 7000), equipped with an EDS (INCA PentaFET-x3), was used for the analysis of the samples. TEM was carried out with a Philips CM-120 instrument operating at 120 kV equipped with an energy-dispersive X-ray analyzer (EDS). HRTEM was performed with an FEI Tecnai F30-UT microscope operating at 300 kV. All powders that were analyzed by electron microscopy were dispersed in ethanol, using an ultrasonic bath, and the suspension was dripped on lacey carbon/Cu grids.

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Author Contributions

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## Notes

The authors declare no competing financial interest.
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