Unveiling the Structure of MoS$_x$ Nanocrystals Produced upon Laser Fragmentation of MoS$_2$ Platelets

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Supporting Information

ABSTRACT: Transition-metal dichalcogenide MoS$_2$ nanostructures have attracted tremendous attention due to their unique properties, which render them efficient nanoscale functional components for multiple applications ranging from sensors and biomedical probes to energy conversion and storage devices. However, despite the wide application range, the possibility to tune their size, shape, and composition is still a challenge. At the same time, the correlation of the structure with the optoelectronic properties is still unresolved. Here, we propose a new method to synthesize various morphologies of molybdenum sulfide nanocrystals, on the basis of ultrashort-pulsed laser fragmentation of MoS$_2$ platelets. Depending on the irradiation conditions, multiple MoS$_x$ morphologies in the form of nanoribbons, nanospheres, and photoluminescent quantum dots are obtained. Besides the detailed structural analysis of the various crystals formed, the structure–property relation is investigated and discussed.

1. INTRODUCTION

Transition-metal dichalcogenides (TMDs) are unique two-dimensional (2D) materials due to their fascinating electronic, optical, and catalytic properties. The MoS$_2$, in particular, is a typical TMD comprising weakly bonded S–Mo–S sandwiched layers. A single MoS$_2$ layer exhibits remarkably different properties than those of the bulk; the most pronounced one is that it is a direct-band gap semiconductor contrary to the bulk, which shows an indirect band gap of 1.22 eV. Their unique properties render them efficient nanoscale functional components for various applications, including sensors, biomedicine, and energy conversion and storage devices.

Besides this, zero-dimensional (0D) TMDs have been found to exhibit high stability and extraordinary optoelectronic properties due to quantum confinement effects. Such low-dimensional materials found numerous applications in electrochemical photocatalysis, bioimaging, and optoelectronic devices. MoS$_2$ nanomaterials, in particular, have been synthesized with different methods, such as ionic liquid-assisted grinding exfoliation, hydrothermal routes, electrochemical exfoliation, colloidal methods at high temperature, laser ablation in liquids, and via an induced Fenton reaction. Among them, the grinding exfoliation and the hydrothermal methods are time-consuming, considering that the first requires multiple centrifugation steps for the size selection of the particles whereas the second demands 18 h of reaction at 220 °C. Besides this, the electrochemical methods are two-step procedures and use hazardous materials.

Finally, the wet chemistry synthesis requires complex apparatus such as a Schlenk line and continuous inert gas flow during the reaction and takes place at high temperature, which increases the time and cost of the final products.

The shape of the MoS$_2$ nanocrystals synthesized via the methods developed to date, is centrosymmetric, whereas the possibility to tune their size, shape, and composition is still a challenge. In this work, we propose a simple and rapid photoinduced method to control the morphology and stoichiometry of MoS$_x$ nanostructures, via ultrashort-pulsed laser irradiation of MoS$_2$ platelets, in solution. It is a single-step, room temperature, and green process, providing different nanocrystal morphologies without the need of hazardous materials and additional surface functionalization. Besides this, it allows fundamental studies of the impact of crystal structure and morphology on the physicochemical properties of the MoS$_x$ nanostructures. The rather simple and scalable method under ambient conditions provides unique opportunities for the cost-effective synthesis of bulk amounts of nanostructures with controllable size, shape, and stoichiometry.

2. RESULTS AND DISCUSSION

The initial colloidal solution of platelets has been prepared by laser ablation of a MoS$_2$ powder pellet in deionized water. For this purpose, a 513 nm laser source, emitting 170 fs pulses with a repetition rate of 60 kHz, has been used (Figure S1). The platelet colloids obtained by this process were stable in water for months at ambient conditions. Subsequently, the aqueous
solution of MoS$_2$ platelets was irradiated using a 1030 nm laser source, emitting 170 fs pulses with a high repetition rate of 75 MHz (Figure 1b).

The influence of the irradiation time, ranging from 0 to 10 000 s, on the morphological and structural evolution of the of MoS$_x$ nanostructures attained (Figure 1a) was carefully examined by TEM and Raman experiments. Representative, bright-field low-magnification TEM images for all structures obtained are presented in Figure 1c. In particular, the initial colloidal solution before the irradiation comprises bulk-like platelets, which have been ablated from the MoS$_2$ target. Following 100 s of irradiation, the as-prepared platelets become thinner (nanosheets), as indicated by the lighter contrast exhibited in the respective TEM images, while their lateral size becomes smaller. At 300 s of irradiation, nanoribbons of 20−50 nm width and length similar to that of the nanosheets prepared at 100 s are formed. Finally, above 1000 s of irradiation time, nanospheres are formed, with sizes down to 5 nm; the higher the exposure time, the lower is the mean nanosphere diameter produced.

Raman spectroscopy was used to probe the vibrational properties of the different structures formed. As shown in Figure 2, the two Raman peaks associated with $1E_{2g}$ (in-plane motion of Mo and S in opposite directions) and $A_{1g}$ (out-of-plane motions of S atoms) active modes are observed in all cases. In particular, for the nanosheets formed at 100 s, the two peaks are centered at 383.2 and 407.8 cm$^{-1}$ (Table S1), in accordance to previous reports on bulk MoS$_2$. Upon transition from nanosheets to nanoribbons and nanospheres, a characteristic blue shift and broadening of both peaks were observed. The blue shift is 3.4 cm$^{-1}$ for the $1E_{2g}$ and 2.1 cm$^{-1}$ for the $A_{1g}$ for the nanosheet-to-nanoribbon transition. According to the literature, the thinning of bulk MoS$_2$ to ultrathin nanosheets comprising three layers leads to a blue shift of the $1E_{2g}$ and $A_{1g}$ modes of about 0.6 and 2.1 cm$^{-1}$,
respectively. In addition, the broadening of these peaks has been associated with the decrease in the number of layers. On the basis of these findings, the large blue shift of the $^1E_{2g}$ mode could not be solely attributed to the nanostructures thinning; therefore, another structural parameter could also play a role (Figure 3). No significant shift was observed, for both modes, upon the transition from nanoribbons to nanospheres. However, the transformation of nanospheres to quantum dots gives rise to a further blue shift for both modes, namely, 4.9 for the $^1E_{2g}$ and 4 cm$^{-1}$ for the $A_{2g}$ respectively. This observation is in contrast to the majority of literature results on Raman spectra of MoS$_2$ nanostructures. For example, a red shift of the in-plane mode has been observed in monolayered structures of nanosheet or quantum dot morphologies. A large blue shift has been found only in the case of quantum dots prepared with anionic liquid-assisted grinding exfoliation process, associated with disorder at the particles edges. In addition, such large shift of the $^1E_{2g}$ mode (2.1 cm$^{-1}$ per % strain) has been found in strained MoS$_2$ structures. The shift is larger in the case of few-layered structures (2.1 cm$^{-1}$ per % strain) compared with monolayered ones (1.7 cm$^{-1}$ per % strain).

Furthermore, there are three different mechanisms that would explain the asymmetric broadening of the Raman peaks: (1) The broadening in the nanocrystalline materials is described by the phonon confinement model, which leads to a breakup of selection rules, meaning, also, non-zone-center phonons will participate in scattering. (2) The size/shape of the spectral lines is changing due to size effects of the grown nanostructures. (3) The crystallinity of the material could affect the broadening of the peaks. A well-crystalline material yields a spectrum with very sharp, intense Raman peaks, whereas an amorphous material will show broader less intense Raman peaks. These two states (e.g., fully amorphous or fully crystalline) can be considered as spectral extremes, and a Raman spectrum from an intermediate state (e.g., partially crystalline) will have characteristics that are intermediate in terms of peak intensity and width (sharpness). On the basis of the Raman spectroscopy findings on disordered particles and strained layered structures and the three main mechanisms that could affect the broadening of the peaks stated above, we may postulate that apart from the reduction in the number of atomic layers, the laser-induced structural changes give rise to remarkable strain and disorder effects.

High-resolution transmission electron microscopy (HRTEM) analysis was used to evaluate the formation mechanism of the various kinds of nanostructures obtained. In particular, the following was observed.

2.1. For nanoribbons. HRTEM imaging revealed that the nanoribbons prepared upon 300 s of irradiation are crystalline (Figure 4) and have a width of $w = 31.6 \pm 11.1$ nm (Figure S2a). The corresponding FFT patterns for the selected areas marked by rectangles in the middle (blue) and at the edge (red) of the nanoribbon are also presented. The zone axis in the image corresponds to the $[101]$ direction. The indexing has been assigned according to the reference pattern of the monoclinic Mo$_2$S$_3$ structure (ICSD, #073453).

![Figure 3. Peak position of the $^1E_{2g}$ and $A_{2g}$ Raman modes, extracted by fitting the peaks in the Raman spectra with a Gaussian curve, for the different morphologies obtained ranging from platelets to quantum dots.](https://example.com/fig3)

![Figure 4. HRTEM image of an individual nanoribbon. The corresponding FFT patterns for the selected areas marked by rectangles in the middle (blue) and at the edge (red) of the nanoribbon in Figure 4, cannot be indexed with the hexagonal structure of the MoS$_2$ (ICSD, #049801). The structure is compatible with the monoclinic structure of the Mo$_2$S$_3$ (ICSD, #073453), as the measured lattice spacings for the (111) and (101) are 2.8 and 4.4 Å, respectively. The corresponding Mo$_2$S$_3$ polymorph has been found in the literature to be formed due to surface phase transformation upon thermal annealing of MoS$_2$ at a temperature up to 1300 K or by sputtering of MoS$_2$ films with low-energy Ar$^+$ ions. Besides this, irradiation of MoS$_2$ monolayers with an electron beam leads to the introduction of sulfur vacancies. Finally, the Mo$_2$S$_3$ phase was found in nanodots synthesized by the arc-melting method at 3000 °C, followed by a ball milling process. To further shed light on the structural features of the nanoribbons, we compared the FFT pattern calculated from an area in the middle to that at the edge of an individual nanoribbon (Figure 4). Although the central part is well-crystalline and there is no evidence for grain boundaries, the FFT pattern corresponding to the nanoribbon edge revealed the presence of disorder; the observed streaking in diffraction spots, in particular, indicates the existence of a stacking fault area along the $b$ axis.

2.2. For nanospheres. Following 1000 s of laser irradiation, nanospheres of $d = 36.2 \pm 10.9$ nm in diameter (Figure S2b) have been formed. HRTEM analysis revealed the presence of different types of particles. The majority are single-phase twinned particles (Figure S5a), and a relatively small number of fullerene-like or amorphous particles (Figures S5b and S5) has been additionally observed. Fullerene particles have been found using a similar laser-ablation technique in aqueous solution. FFT pattern analysis revealed the crystal structure of the single-phase particles, which is compatible with the monoclinic structure of the Mo$_2$S$_3$ (ICSD, #073453). Indeed, lattice fringes with interplanar spacings of 3.0 and 2.2 Å have been identified, which are assigned to the (200) and (210) of the monoclinic crystal Mo$_2$S$_3$ structure, respectively. It should be noted here that the crystal structure of such nanocrystals is the same as that of the nanoribbons, although a...
small percentage of nanoparticles exhibit the rhombohedral crystal symmetry of the MoS\(_2\) (Figure S3). The coexistence of these two phases in the same sample has been also found in previous reports.\(^{40}\) The mixture of several molybdenum multisulfides has also been confirmed from the stoichiometry found by energy-dispersive spectrometry (EDS) analysis in different areas of the sample (Figure S4). This stoichiometry was found to be MoS (1:1), which is far away from the stoichiometry Mo/S = 1:2 of the MoS\(_2\) target. Upon careful inspection of the HRTEM images and the corresponding FFT pattern, it can be concluded that the particles exhibit a quasispherical morphology of the twined type, revealed by the additional spots between the spots of the monoclinic phase. Variation of the Mo/S ratio in MoS\(_2\) crystal structures has been found in the literature that it is associated with the presence of S vacancies.\(^{42}\) Twin defects, dislocations, and grain boundaries in the crystal structure are accumulated by sulfur vacancies.\(^{43,44}\) A ratio of 1.2 found in substoichiometric bilayers of MoS\(_2\) due to lattice distortion originated from exfoliation process using hydrazine salts.\(^{45}\)

### 2.3. For the quantum dots.

Quantum dots with diameter \(d = 6.5 \pm 1.6\) nm (Figure S2c) are formed above 10 000 s of laser irradiation. Selected area diffraction analysis of a random area of the quantum dot sample (Figure S6) revealed the crystal structure of the quantum dots, which is compatible to the monoclinic crystal structure of MoS\(_2\) (Figure 6a). No indication for molybdenum oxide has been found due to possible oxidation of the surface.\(^{46–48}\) This conclusion is in good agreement with the Raman spectra at the higher shift region. Peaks at 666 and 820 nm that could be assigned to the stretching modes of the triply coordinated oxygen (Mo\(_3\)−O) and the doubly coordinated oxygen (Mo\(_2\)−O) of the a-MoO\(_3\) phase\(^{49,50}\) are found only for the case of the nanospheres (Figure S7). The corresponding FFT pattern calculated from the HRTEM images (Figures 6b and S8) indicated a twinned structure.

Notably, the quantum dots are photoluminescent at room temperature upon their excitation by a 248 nm laser beam (Figure 6c). In particular, a single PL peak is observed centered at 448 nm whereas no additional peaks are observed at longer wavelengths, indicating the absence of quantum dot aggregation. A similar spectrum has been recorded for the nanospheres (Figure S9). The main features are similar, but the spectrum of the nanospheres is blue-shifted compared to that of quantum dots. This is a contradictory result if we consider the particle size of the two samples. This is due to the existence of different particles (mainly of MoO\(_3\)) in the sample of the nanospheres.

Similar spectra have been recorded for water soluble 1,4-diaminobutane-functionalized MoS\(_2\) quantum dots of about 5 nm synthesized by a bottom-up approach.\(^{51}\)

On the basis of the above analysis, we may speculate on the formation mechanism that accounts for the structure and shape evolution of the various MoS\(_2\) nanostructures observed (Figure 7). Initially, laser irradiation of MoS\(_2\) platelets gives rise to the photoinduced exfoliation to form few-layered nanosheets. The subsequent irradiation of nanosheets leads to the photoinduced unzipping\(^{52–54}\) of the nanosheets’ edges to form nanoribbons, which are crystalline in the Mo\(_2\)S\(_3\) structure, exhibiting structural defects at their edges. This explanation complies with previous reports, where the Mo\(_2\)S\(_3\) polymorph was found at the edges of MoS\(_2\) nanosheets.\(^{37}\) Upon further irradiation, the nanoribbons transform in nanospheres through a laser-induced melting and subsequent resolidification.\(^{41,55}\) The temperature in the irradiated area due to the laser energy absorption is increased above the melting point of the material, and melted MoS\(_2\) droplets are formed. The resolidification occurs when the surface temperature of the droplets reduces below the melting point of MoS\(_2\).

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4.2.1. Transmission Electron Microscopy (TEM). Low-stirrer. The synthesis is reproducible, but the yield is low.

3. CONCLUSIONS

In summary, this work illustrates that laser irradiation of MoS2 bulklike platelets could be used as an effective way for the synthesis of different morphologies of molybdenum sulfides. This approach is simple, scalable, performed under ambient conditions, and can therefore be useful for the cost-effective synthesis of bulk amounts of nanostructures with controllable size, shape, and stoichiometry. More important, the various nanocrystal morphologies can be produced without the need of hazardous chemicals and additional surface functionalization processes, which make this technique appealing for many potential applications.

4. MATERIAL AND METHODS

4.1. Preparation of the Different Colloids. 4.1.1. Production of the Aqueous Solution of MoS2 Platelets. Initially, a MoS2 target has been prepared via pressing MoS2 powder into a pellet of 15 mm diameter. This target was placed at the bottom of a glass vial and immersed into 2 mL of deionized water. Subsequently, the beam of a Yb:KGW femtosecond laser was focused through the water layer, onto the target to exfoliate the MoS2 powder into platelets (Figure S1). The laser wavelength, the repetition rate, the pulse duration, and the power used for this purpose were 513 nm, 60 kHz, 170 fs, and 90 mW, respectively. The total ablation time was 10 min. During laser irradiation, the target was continuously rotated using a rotation stage. All solutions obtained after irradiation were centrifuged at 1500 RPM for 10 min. Then, the supernatant colloidal solution is placed in a quartz cuvette for subsequent irradiation.

4.1.2. Synthesis of MoS2 Nanostructures (Figure 1). The as-prepared aqueous solution of the MoS2 platelets was divided into 5 equivalent aliquots. Then, each aliquot was irradiated for 100, 300, 1000, 3000, and 10 000 s, respectively, using the same laser system, although at different irradiation parameters. In this case, the wavelength, the repetition rate, pulse duration, and power used were 1026 nm, 75 MHz, 170 fs, and 4 mW, respectively. During the irradiation process, the colloidal solution was continuously agitated via use of a magnetic stirrer. The synthesis is reproducible, but the yield is low.

4.2. Characterization of the Colloidal Solutions. 4.2.1. Transmission Electron Microscopy (TEM). Low-magnification and high-resolution TEM (HRTEM) images were recorded on a JEOL 2100 transmission electron microscope, operating at an accelerating voltage of 200 kV. For the purposes of the TEM analysis, a drop of the aqueous colloidal solution was deposited onto a carbon-coated copper TEM grid and then the solvent was allowed to evaporate. All images were recorded by a Gatan ORIUS SC 1000 CCD camera, whereas the structural features of the nanostructures were studied by two-dimensional (2D) fast Fourier transform (FFT) analysis.

4.2.2. Raman Spectroscopy. Raman measurements were performed at room temperature using a Horiba LabRAM HR Evolution confocal micro-spectrometer, in backscattering geometry (180°), equipped with an air-cooled solid-state laser operating at 532 nm, with 100 mW output power. The laser beam was focused on the samples using a 50X Olympus microscope objective (numerical aperture of 0.50), providing a ~22.5 mW power on each sample. Raman spectra over the 10–3000 cm−1 wavenumber range (with an exposure time of 20 s and 5 accumulations) were collected by a Pelletier cooled CCD (1024 × 256 pixels) detector at ~60 °C, with a resolution better than 1 cm−1 achieved thanks to an 1800 grooves/mm grating and an 800 mm focal length. Test measurements were carried out using different optical configurations, exposure time, beam power, and accumulations to obtain sufficiently informative spectra using a confocal hole of 100 μm but ensuring to avoid alteration of the sample, whereas the high spatial resolution allowed us to carefully verify the sample homogeneity. The wavelength scale was calibrated using a Silicon standard (520.7 cm−1), and the acquired spectra were compared with scientific published data and reference databases, such as Horiba LabSpec 6 (Horiba).

4.2.3. Laser-Induced Fluorescence (LIF) Spectroscopy. Each solution was placed in quartz cuvette without further dilution, and the respective PL spectra were recorded at room temperature. For sample excitation, a KrF excimer laser, operating at 248 nm has been utilized. The pulse duration was about 20 ns, the excitation energy ~3.2 mJ, and the laser beam diameter 9.0 mm (fluence ~5 mJ/cm2). The fluorescence measurements were performed at room temperature and recorded by a monochromator (PTI Technology) that is connected with an Andor iStar 734 Series Intensified Charge Coupled Device. The fluorescence signal of the samples was collected and guided to the spectrograph by an optical fiber.

4.2.4. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS). EDS (JEOL 7000), equipped with an EDS (INCA PentaFET-x3), was used for the analysis of the samples. These experiments were performed on solid-state samples produced after drying a small volume of the corresponding colloidal solution on a piece of a single-crystalline silicon wafer.
EDS analysis, TEM images, size distributions, Raman spectra, PL curves and scheme of the setup for the laser ablation of the flakes in liquid media (PDF).

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