Room Temperature Micro-Photoluminescence Studies of Colloidal WS_2 Nanosheets

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Summary. Wet-chemical syntheses of quasi two-dimensional (2D) transition metal dichalcogenides (TMDs) are emerging as promising methods for straightforward solution processing and upscaling of the materials. However, the photoluminescence (PL) properties of colloidal TMDs are virtually unexplored due to typically non-emissive TMD synthesis products. In this project, we demonstrate the first room temperature micro-PL characterization of delicate colloidal ultrathin colloidal WS_2 nanosheets, rendering the wet-chemical synthesis as a simple and versatile alternative to existing methods including exfoliation and chemical vapor deposition (CVD).

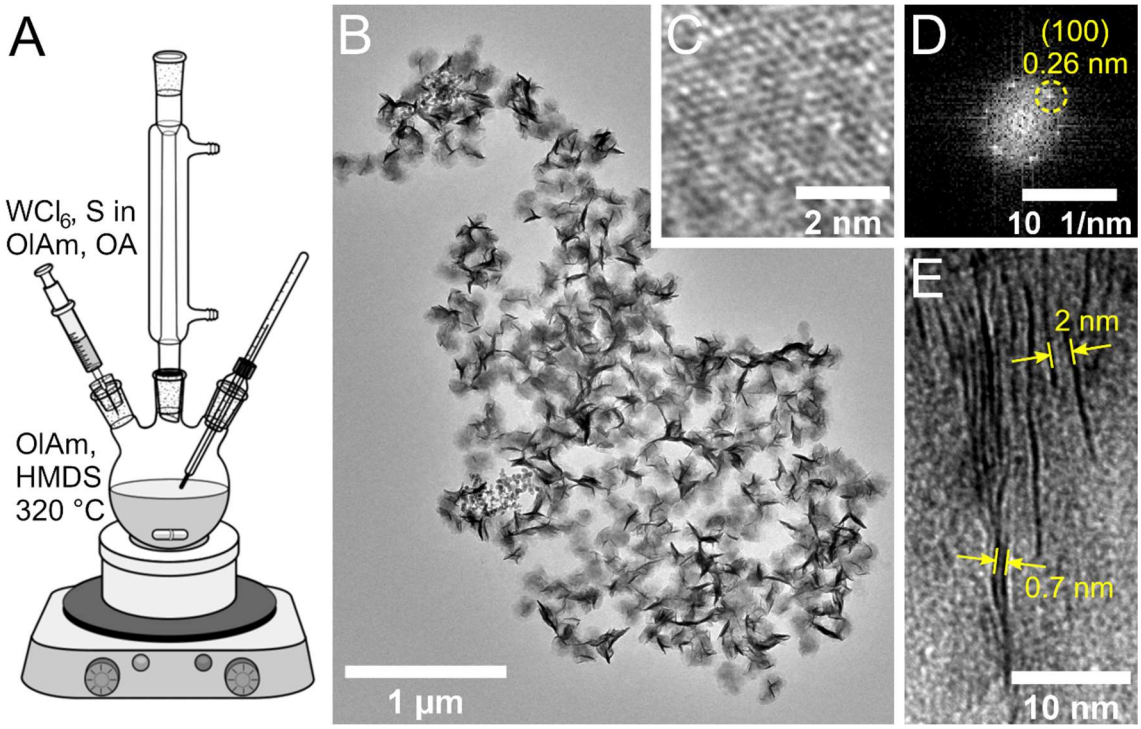

Figure 1: (A) Schematic of the wet-chemical synthesis. Overview TEM (B) and HR-TEM image (C) of colloidal WS_2 nanosheets. (D) FFT image underpinning the hexagonal periodicity of the nanosheets. (E) TEM image revealing layer distances with and without interlayer ligands of 0.73 ± 0.06 nm and 2.4 ± 0.4 nm.

Photoluminescent colloidal WS_2 nanosheets were synthesized using a wet-chemical synthesis pathway for obtaining semiconducting WS_2 mono- and few layers (Figure 1A). A superior solubility of the tungsten precursor (WCl_6) was achieved by dissolving WCl_6 in a mixture of oleylamine (OlAm) and oleic acid (OA). The formed oleylammonium species in this acid-base equilibrium assembles as a lamellar tungsten precursor and leads to enhanced process control. In contrast to previously described WS_2 nanosheet syntheses, less toxic elemental sulfur dissolved in OlAm was used as the chalcogen source. By combining both precursor solutions and successively adding them to OlAm and hexamethyldisilazene (HMDS) at 320 °C *in situ* H_2S was formed which reacts with the tungsten precursor to yield WS_2 nanosheets.

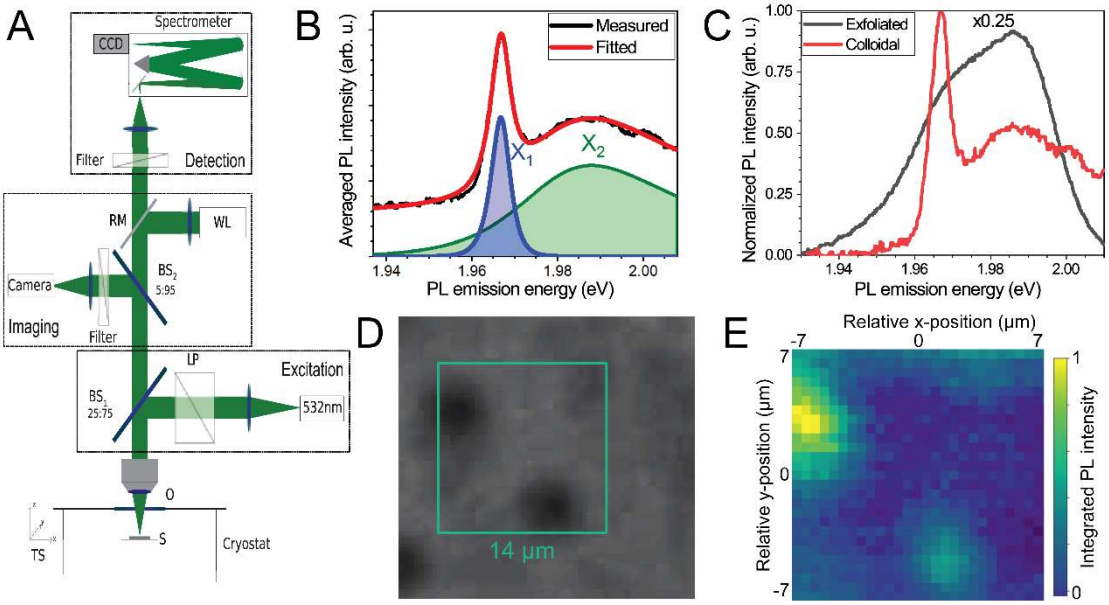

Figure 2: (A) Simplified schematic of the µ-PL setup including the following abbreviations: BS (beam splitter), CCD (charge-coupled device), LP (linear polarizer), O (objective lens), RM (removable mirror), S (sample), TS (translation stages) and WL (white light source). Monolayer PL of colloidal WS_2 nanosheets fitted with asymmetric hyperbolic secant functions (B; X_1: Trion and X_2: Neutral exciton) and compared to an exfoliated WS_2 monolayer (C). Microscope image of separated WS_2 multilayer features (D) with the associated PL map (E).

The obtained colloidal WS_2 nanosheets were structurally characterized by transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), powder X-ray diffraction (XRD) and absorption measurements. The characterization confirmed an overall flowerlike morphology (Figure 1B), a high crystallinity (Figure 1C), the hexagonal periodicity (Figure 1D) and the presence of mono- and multilayer nanosheets (Figure 1E) with a semiconducting crystal phase.

Up to now, typical colloidal TMDs exhibited no PL due to a high number of chalcogen vacancies. In our study we used a highly sensitive confocal microscope setup (Figure 2A) to investigate the optical properties of colloidal WS_2 nanosheets. In conjunction with the absorption and TEM measurements we observed both mono- and multilayer µ-PL for the first time in these structures. The colloidal monolayer PL exhibits three contributions (Figure 2B) and promisingly similar properties compared to a state-of-the-art exfoliated sample (comparison in Figure 2C). Additional characterization included spatially resolved measurements (Figure 2D and Figure 2E) as well as the determination of a convincing long-term air-stability of the WS_2 nanosheets and a photodegradation process that will be investigated in future research.

Our systematic investigation of the joint structural and µ-PL properties of colloidal TMDs advances the materials into a competitive level with conventionally produced 2D TMDs and enables a variety of follow-up research to further optimize the optical properties of these delicate 2D structures.

For further information see:

A.P. Frauendorf, A. Niebur, L. Harms, S. Shree, B. Urbaszek, M. Oestreich, J. Hübner, J. Lauth, *Room Temperature Micro-Photoluminescence Studies of Colloidal WS2 Nanosheets*, **J. Phys. Chem. C**, 2021, **125**(34), 18841-18848, https://doi.org/10.1021/acs.jpcc.1c06240