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Bottom-up Synthesis, Reactivity, and Simulation of Freestanding 2D Transition Metal Chalcogenide (TMC) Nanostructures

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14. ABSTRACT
The PI has successfully accomplished the four specific aims as planned in the research proposal in the are of 2D layered TMC nanostructures that include: development of solution based synthetic protocols, computational screening of intrinsic properties, size control, and elucidation of chemical interaction and properties of edges and basal planes. The PI has developed and published a solution based synthetic protocol for single layer MSe2 nanosheets. The PI has published 4 peer reviewed journal articles to date with this research grant.

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"Bottom-up Synthesis, Reactivity, and Simulation of Freestanding 2D Transition Metal Chalcogenide (TMC) Nanostructures"

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The project has been carried out in my capacity as Adjunct Professor at Jacobs University Bremen. The web site and phone number points at my present affiliation at Leipzig University.

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I. Abstract

Two dimensional (2D) layered transition metal chalcogenide (TMC) are emerging fast due to their unique characteristics ranging from electron transport, magnetism, intercalation chemistry and catalytic and optical properties. Until now, most developments have been focused on device fabrications and their physical performance tests. Although the understanding of the chemical nature of 2D TMCs is critical for the success in practical applications (*e.g.*, nanodevice, energy storage/conversion, sensing and catalysis), the research on chemical aspects such as surface modification, bottom-up synthesis, and reactivity of 2D TMC nanostructures is yet scarce. In this project, we have investigated the chemistry of 2D TMCs such as anisotropic reaction on surface (*e.g.*, edge or basal plane) and molecular induced electronic structural effects (*e.g.*, nucleophile or electrophile) by experimental and computational approaches. Based on the understanding of chemistry of 2D TMCs, we successfully controlled the size, thickness, and morphology of 2D TMC nanosheets in the solution phase.

Specific Aims:

1. ***Development of solution based synthetic protocols*** that can be generally applicable for a wide variety of metals and chalcogens (e.g. metals in group IV, Ti, Zr, Hf; group V, Nb; group VI, Mo, W; group VIII, Pd, Pt with chalcogens of S and Se).
2. ***Computational screening of intrinsic properties*** of all pristine 2D layered TMC materials using density-functional theory (DFT), including stability, doping effect, thermal and electronic properties (i.e. dielectric constant, UV/Vis spectrum and exciton Bohr radius), and their size confinement.
3. Development of synthetic and theoretical principles for the ***size control (lateral size and number of layers)*** to examine such confinement effects for electronic/optical/catalytic properties, supported by theoretical and experimental studies.
4. Elucidation of ***chemical interactions and properties of edges and basal planes***. Interaction of 2D TMC edges and basal planes with electron donating or withdrawing chemical species such as Lewis acid/base and radicals with consideration of factors from Pearson’s acid/base concept, metal affinity to steric effects are studied. Edge/basal plane composition and platelet size will be studied employing DFT, aiming at understanding of crystal growth processes and reactivity of TMC nanostructures.

II. Introduction

2D layered TMC nanostructures are emerging rapidly due to their unique chemical and physical properties that are difficult to obtain or absent in other 2D materials such as graphene. For example, MoS_2 nanosheets are known for their exceptional device performance with high signal-to-noise (S/N) ratios and optoelectronic capabilities.[1] TMCs, with the formula of M_nX_m (M= Ti, Zr, Hf, Mo, W, Ni, Pd, Pt ;X=S, Se, Te; n, m=1, 2, 3...), have a variety of unique anisotropic characteristics ranging from charge transport to magnetism, intercalation, and catalytic and optical properties.[2] Nanoscale confinement, such as single sheet formation or lateral size reduction, of 2D TMC materials is expected to yield new scientific understanding and many potential applications.[3] Until now, major developments in both the generation of TMC nanostructures and study of device physics, have been limited to the gas phase CVD or exfoliation techniques.[4] In contrast, the research on chemical aspects such as surface modification, bottom-up synthesis, and reactivity of TMC nanostructures is very scarce.[5] Due to their high surface-to-volume ratio, open-gap structures and the presence of different coordination states on the edge and basal planes,[6] TMC nanostructures are chemically sensitive to their environment (Figure 1). For example, upon exposure to mild chemical environments, TMC nanostructures can be susceptible to chemical adsorption with the concurrent modification of physicochemical properties including electronic structure, charge transfer rate, and catalytic efficiency.[7] Meanwhile, under highly reactive chemical environments, TMCs can readily react with the surrounding chemicals to make insertion/addition of elements, ion exchange, dissolution to form entirely new nanostructures and compositions that are different from the original TMC nanostructures.

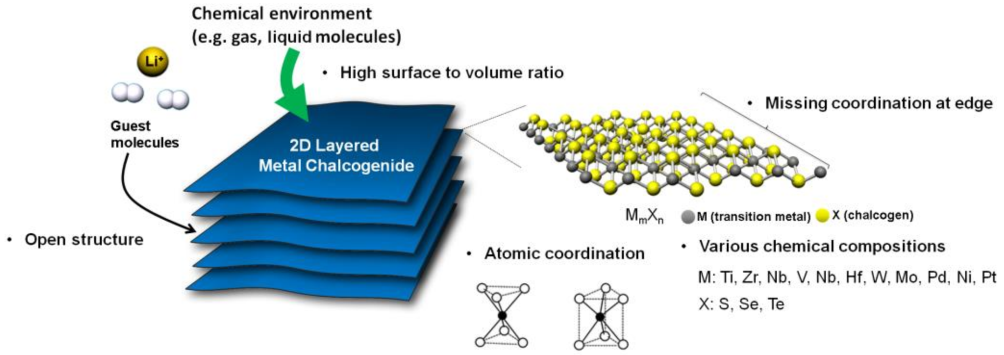

Figure 1. Unique characteristics of 2D layered TMC nanostructures. Structural features including high surface-to-volume ratio, missing coordination at edge, and open structure make 2D TMCs sensitive to their chemical environments. In addition, 2D TMCs have versatile physicochemical properties, for instance, their electronic character ranges from metallic to semimetallic or semiconducting due to the variety of compositional/structural combinations and atomic coordination. Within each layer of TMC nanostructures, atoms are covalently bonded whereas the individual layers are bound by van der Waals interaction.

III. Approach:

In this study, we first aimed to develop the bottom-up chemical synthetic protocols for free standing 2D layered TMC nanostructures with controlled lateral size and thickness. The ability to modulate the size and thickness of these materials allowed us to identify new phenomena associated with their electronic/optical/catalytic properties. In fact, with the prepared freestanding 2D layered TMC nanostructures, an effective method to synthesize high-quality and size-controlled single layered TMC quantum dots via intercalation induced exfoliation from multilayer quantum dots (MQDs) precursors was accessed to define the role of lateral confinement on the optical properties of the 2D exciton. The third component of this project, achieved by state-of-the art computer simulation, was the development of the theoretical background for understanding the size and shape dependent materials properties, reactivities, and activation energy barriers of freestanding TMC nanostructures for structural stability and chemical interactions.

IV. Experimental method

Chemical synthesis of 2D layered TMC nanosheets for its size/thickness control

The solution-based synthesis of 2D layered TMCs was developed following a general synthetic scheme: a reaction medium is first heated to a sufficient temperature (usually from 150 to 300 °C) such that the precursors decompose into monomers at a supersaturated level. After the burst of nucleation seeds, spontaneous crystal growth occurs by consumption of the monomers. [8] Finally, the desired size and shape of nanostructures are achieved by surface stabilization by organic surfactants.[9] One of the key assets of bottom-up chemical synthesis is the simplicity in control of size, shape and composition by analytical adjustment of the reaction parameters such as time, temperature, concentration and choice of reagents. For example, appropriate selection of organic surfactants, in which one binds tightly to the specific surfaces of nanocrystal, thereby hindering growth, results in size control of the final 2D TMC nanosheets.

Absorption spectroscopy

The single-particle photoluminescence (PL) spectra from as-synthesized single- or multi-layered nanosheets were measured with a wide-field microscope equipped with an imaging spectrograph and an electron multiplying charge-coupled device.[10] A Xe-lamp in conjunction with a monochromator provides the tunable excitation light in the UV−vis region. Excitation of as-synthesized colloidal TMC nanosheets was performed via an ATR scheme using a quartz prism to minimize the interference from the excitation light during the PL measurement. A highly diluted colloidal suspension was drop casted onto a thin quartz plate and the placed on top of the prism using an index matching liquid. The PL from specimen was collected with an objective focused on the EMCCD either as an image or as a spectrum using a tube lens through the imaging spectrograph. The PLE spectra were obtained by measuring the integrated PL intensity as a function of the excitation wavelength with a 10 nm bandwidth after a spectral calibration of the entire optical system with CdSe quantum dots, which have a well-known PLE profile.

Theoretical modelling

Density-Functional Theory (DFT) has become an established tool to understand the intrinsic properties of 2D TMCs, including structure, vibrational, electronic and optoelectronic properties. [3a, 11] For deposited or multi-layer 2D TMCs, caution is needed when addressing the interlayer interactions, as London dispersion is lacking in DFT, and a correct interlayer distance is crucial for predicting most properties. For most TMC nanostructures, however, these distances can, be obtained from experiment, by higher-level calculations (i.e. LMP2), by employing semi-empirical corrections[12] or the harmonic oscillator model describing many-body effects.[13] It should be noted that relativistic effects can play an important role in 2D TMCs, in particular in the upper regions of the valence band and thus affecting the optical properties significantly. Accounting for spin-orbit effects is state-of-the-art today, but increases the computational effort. DFT is an excellent tool to determine the reactivity of molecules, directly relating to Pearson's Hardness/Softness Acid/Base (HSAB) principle, and with the possibility to assign activated electrons to orbitals and to spatial regions.

V. Results and Discussion:

Hexagonal transition-metal chalcogenide nanoflakes

We have explored the rationale behind the hexagonal shape of group IV TMC nanoflakes.[14] We have found that a low-energy structure of these particles always follow the formula M_nX_{n-2}, thus leaving 4 excess electrons that are distributed over the platelet and which are responsible for the lateral quantum confinement effect. The hexagonal shape is rationalized by minimizing the number of edge atoms with respect to basal plane atoms and, at the same time, keeping only low-energy edge structures.

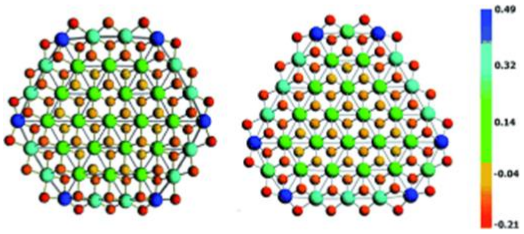

Figure 2. Partial atomic-charge distribution in Ti_{37}^{Hex} and Ti_{36}^{Tri}obtained from a multipole derived charge analysis (mdc-q).

Colloidal synthesis of single layer MSe$_2$ (M= Mo and W) nanosheets

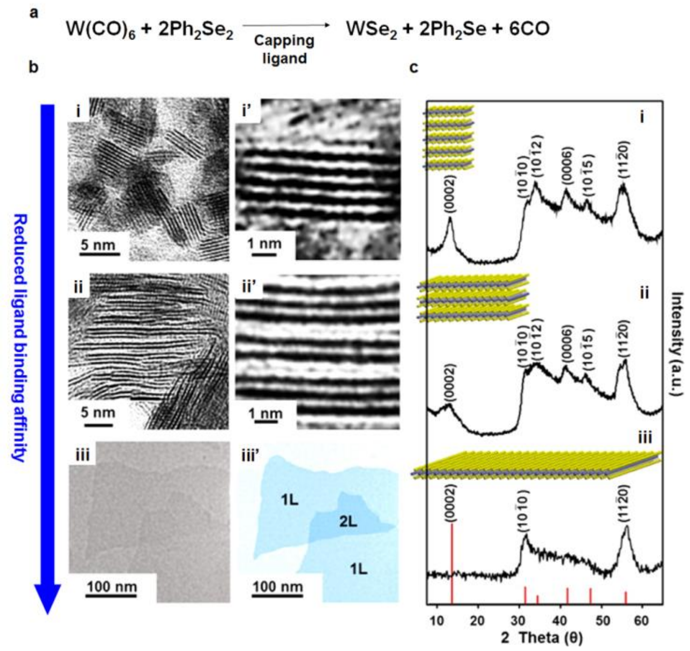

Figure 3. Thickness-controlled synthesis of WSe$_2$ nanosheets with the use of different binding affinity ligands. (a) Chemical equation for synthesis of WSe$_2$ nanosheets. (b) TEM images of WSe$_2$ nanosheets synthesized with (i) oleylamine, (ii) oleyl alcohol, and (iii) oleic acid. (i′, ii′) Magnified TEM images of the nanosheets and (iii′) pseudo-colored image of the single-layer nanosheets. (c) XRD patterns of WSe$_2$ nanosheets synthesized with (i) oleylamine, (ii) oleyl alcohol, and (iii) oleic acid.

We have developed a solution based synthetic protocol for single layer MSe$_2$ (M= Mo and W) nanosheets.[15] The key concept is controlling the binding affinity of capping molecules to the reactive edge facets of 2D TMCs. Using this approach, the thickness of the 2D TMCs is controlled from single layer to multilayer. By changing the functional groups of the surfactant ligands from carboxylic acids to alcohols and amines, the number of layers in the nanosheets can be controlled. Single-layer MSe$_2$ nanosheets with lateral sizes of 200–400 nm were obtained when oleic acid was used as a capping ligand, while multilayered nanosheets with lateral sizes below 20 nm were formed from relatively strong ligands, such as oleylalcohol and oleylamine.[98] The computed binding affinities of the ligands toward the metal centers on the edge facets were −1.475, −1.161, and −0.848 eV for methylamine, methyl alcohol, and formic acid, respectively, indicating that strongly bound capping ligands (*i.e.*, oleylamine) stabilize the edge facets and inhibit lateral growth, while the vertical growth of WSe$_2$ nanosheets can competitively occur, leading to smaller but multilayered nanosheets. In contrast, oleic acid, which has a significantly weaker stabilizing effect on the edge facets, promotes the lateral anisotropic growth of single-layer WSe$_2$ nanosheets.

Colloidal Single-layer quantum dots with lateral confinement effects

An alternative route in thickness controlled synthesis from our previous report, lateral size controlled multilayered WSe_2 quantum dot (MQD) was synthesized by gradual changes in precursor to surfactant ratio (**Figure 4a**).[16] The controllability of the lateral size is perhaps a result of the larger population of surfactant (i.e., trioctylphosphine) molecules on the surface of the WSe_2, which decreases the growth rate and thereby produces smaller WSe_2 MQDs. Then, intercalation of linear alkylamines with two different chain lengths was taken place for mild exfoliation process to isolate lateral size controlled single layer quantum dots (SQDs) (**Figure 4b**). The method, so called ‘tandem molecular intercalation’ (TMI) method facilitates efficient exfoliation without sonication or reactive chemicals, such as Li^+ that prevents the formation of potential defects in prepared 2D TMC quantum dots during the exfoliation process. This methodology allowed us to explore the lateral confinement effects on the unique optical properties originating from 2D excitons in single-layer TMCs. The single-particle PLE and PL spectra of WSe_2 SQDs clearly revealed not only the lateral confinement effect on the optical transition energy but also the enhanced vibronic coupling due to the proximity of the edge bonds resulting in a large increase in the Stokes shift and spectral width. Furthermore, single-particle polarization spectroscopy shows that the absorption and emission of colloidal WSe_2 SQDs exhibit the same in-plane, 2D isotropic transition dipole and linear PL polarization anisotropy as those of the 2D exciton in the single-layer sheets of WSe_2. On the other hand, the circular polarization anisotropy observed in single-layer TMC sheets is absent in WSe_2 SQDs, indicating that the valley polarization is lost in the laterally confined single-layer TMCs.

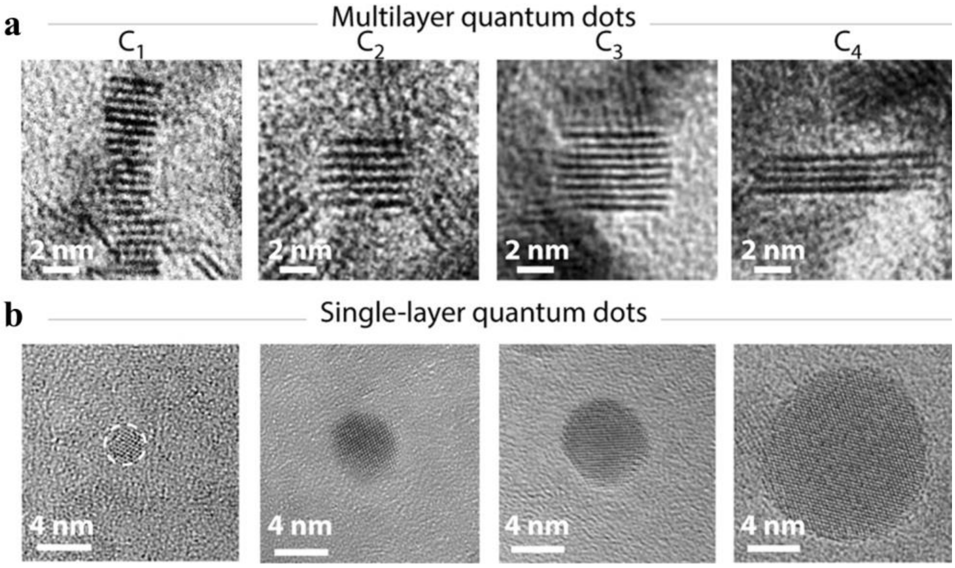

Figure 4. (a) TEM images of the side-view of WSe_2 MQDs and (b) top-view of exfoliated WSe_2 SQDs.

Solvent effect on the optical properties of colloidal single layer WS_2 quantum dots

Based on the spectroscopic analytic techniques acquired from the previous studies, we determined the solvent effect on optical and electronic properties of TMC QDs comparing between mono and multilayer.[17] It was observed that the strong influence of the aromatic solvents on the PL energy and intensity of monolayer WS_2 QD beyond the simple dielectric screening effect, which is considered to result from the direct electronic interaction between the valence band of the QDs and molecular orbital of the solvent (**Figure 5**). It was also observed the large effect of stacking/separation equilibrium on the PL spectrum dictated by the balance between inter QD and QD-solvent interactions.

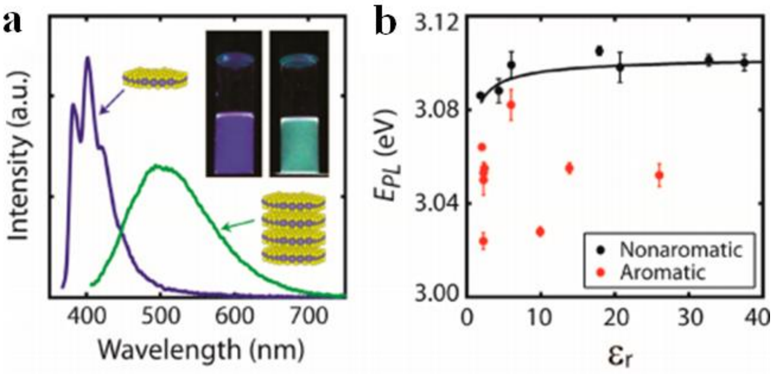

Figure 5. (a) PL spectra of single-layer WS_2 QDs (purple) in DMF and multilayer WS_2 QDs (green) in pentane. (b) PL peak energy of single-layer WS_2 QDs in nonaromatic and aromatic solvents, varying the dielectric constant.

Photo-induced separation of strongly interacting 2D layered TiS_2 nanodiscs

In this study, we showed that the vertically stacked assemblies of TiS_2 nanodiscs present in the colloidal solution due to the strong interparticle interaction *via* basal planes can be

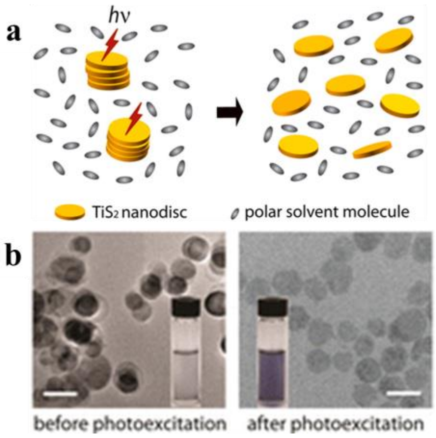

Figure 6. (a) Separation of strongly interacting colloidal 2-D layered TiS_2 nanodiscs via photoinduced weakening of interparticle cohesive energy that facilitates the solvation of each nanodisc. (b) TEM image of the *d* = 150 nm TiS_2 sample before and after 30 min of photoexcitation.

readily separated into individual noninteracting nanodiscs *via* pulsed photoexcitation.[18] Interband photoexcitation of TiS_2 nanodiscs with pulsed laser light creates dense charge carriers that transiently modify the charge distribution within the nanodiscs. The change in charge distribution in TiS_2 nanodiscs during the lifetime of the charge carriers is considered to non-thermally weaken the interparticle cohesive energy and facilitate the solvation of each nanodisc by the solvent molecules

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VII. List of Publications:

i) Ho Jin, Bongkwan Baek, Doyun Kim, Fanglue Wu, James D. Batteas, Jinwoo Cheon, and Dong Hee Son, Effects of Direct Solvent-Quantum Dot Interaction on the Optical Properties of Colloidal Monolayer WS_2 Quantum Dots, *Nano Lett*. **2017**, *17*, 7471, published on October 27, 2017

ii) Ho Jin, Minji Ahn, Sohee Jeong, Jae Hyo Han, Dongwon Yoo, Dong Hee Son, and Jinwoo Cheon, Colloidal Single-Layer Quantum Dots with Lateral Confinement Effects on 2D Exciton, *J. Am. Chem. Soc*. **2016**, *138*, 13253-13259, published on October 3, 2016

iii) Wonil Jung, Sujeong Lee, Dongwon Yoo, Sohee Jeong, Pere Miró, Agnieszka Kuc, Thomas Heine, and Jinwoo Cheon, Colloidal Synthesis of Single-Layer MSe_2 (M = Mo, W) Nanosheets via Anisotropic Solution-Phase Growth Approach, *J. Am. Chem. Soc*. **2015**, *137*, 7266-7269, published on June 8, 2015

iv) Pere Miró, Jae Hyo Han, Jinwoo Cheon, and Thomas Heine, Hexagonal Transition-Metal Chalcogenide Nanoflakes with Pronounced Lateral Quantum Confinement, *Angew. Chem. Int. Ed.* **2014**, *53*, 12624-12628, published on September 11, 2014

v) Daniel Rossi, Jae Hyo Han, Dongwon Yoo, Yitong Dong, Yerok Park, Jinwoo Cheon, and Dong Hee Son, Photoinduced Separation of Strongly Interacting 2-D Layered TiS_2 Nanodiscs in Solution, *J. Phys. Chem. C* **2014**, *118*, 12568-12573, published on May 16, 2014

VIII. List of Presentations:

i) Jinwoo Cheon, Advances of 2D TMC Nanoparticles and Control of Biological Targets with Magnetic Nanostructures, AFRL/RXAN on Wright Patterson Air Force Base, OH, USA, June 10-11, 2015

ii) Wonil Jung, Dongwon Yoo, Sohee Jeong, and Jinwoo Cheon, Colloidal Synthetic Strategy for Anisotropically Controlled Single-Layer 2D Group VI Transition Metal Diselenides, Flatlands Beyond Graphene 2015, Bar Ilan University, Israel, July 7, 2015

iii) Jinwoo Cheon, Chemical Synthesis of Two-Dimensional Transition Metal Chalcogenide Nanostructures, Flatlands Beyond Graphene 2015, Bar Ilan University, Israel, July 9, 2015

iv) Thomas Heine, Transition Metal Dichalcogenide: A Highly Sensitive Species, 1st Conference on Two-Dimensional Layered Materials, Hangzhou, China, October 14, 2014

v) Thomas Heine, Transition Metal Dichalcogenides: Ultrathin Inorganic Materials with Tunable Electronic Properties, MRS 2014 Fall Meeting Boston, USA, December 3, 2014

vi) Thomas Heine, Design of Functional Nanomaterials by Quantum Confinement, Telluride Meeting on Spin-Orbit Coupling, Telluride, CO, USA, June 17, 2015

vii) Thomas Heine, Two-Dimensional Crystals off the Beaten Track: High Coordination Phases and Two-Dimensional Topological Insulators, Flatlands Beyond Graphene 2015, Bar Ilan University, Israel, July 8, 2015

viii) Jinwoo Cheon, Advances of 2D Layered Nanosheets and Magnetic Nanoparticles for Cell Imaging and Activations, Seoul National University, Seoul, Republic of Korea, October 2, 2015

ix) Jinwoo Cheon, Bottom-up Synthesis, Reactivity, and Simulation of Freestanding 2D Transition Metal Chalcogenide (TMC) Nanostructures, Joint US- Korea NBIT-Taiwan Nanoscience Program Review and Technical Exchange on AFOSR/AOARD, USA, October 26-30, 2015
x) Minji Ahn, Sohee Jeong, Dongwon Yoo, Kwan Lee, Pere Miró, Thomas Heine and Jinwoo Cheon, Tandem Molecular Intercalation (TMI) Exfoliation Method for Obtaining Single-Layer Transition Metal Chalcogenides(TMCs), The 3rd Muju International Winter School Series, Muju Deogyusan Resort, Republic of Korea, January 17-21, 2016

xi) Wonil Jung, Dongwon Yoo, Sohee Jeong, Bongkwan Baek, and Jinwoo Cheon, Synthesis of Colloidal Single-Layer Group VI Transition Metal Diselenides via Anisotropic Growth Approach, The 3rd Muju International Winter School Series, Muju Deogyusan Resort, Republic of Korea, January 17-21, 2016

xii) Jeonghee Han, Dongwon Yoo, Sohee Jeong, Jae Hyo Han, and Jinwoo Cheon, Colloidal Synthetic Strategy for Single-layer 2D Transition Metal Chalcogenides (TMCs) Nanosheets, The 3rd Muju International Winter School Series, Muju Deogyusan Resort, Republic of Korea, January 17-21, 2016

xiii) Thomas Heine, Strong Quantum Confinement in Transition Metal Dichalcogenide Bilayers and Two-dimensional Topological Insulators, 2nd International Conference on Two-Dimensional Layered Materials, Hong Kong, January 6-8, 2016

xiv) Thomas Heine, 2016 EMRS Spring Meeting, Session Z, Lille, France, May 2-6, 2016

xv) Thomas Heine, Ultrathin Electronic Devices Tailored by Quantum Confinement, Gordon Research Conference “Two Dimensional Electronics Beyond Graphene”, Mt. Holyoke College, Massachusetts, USA, June 5-10, 2016

xvi) Thomas Heine, Noble Metal Transition Metal Dichalcogenides, Flatlands Beyond Graphene, Bled, Slovenia, July 5-8, 2016

xvii) Thomas Heine, Transition metal chalcogenide 2D nanoflakes made by a surfactant-based approach, International Conference on Solution-based Two-dimensional Nanomaterials(Sol2D16) of NanoGe conference, Berlin, Germany, September 8-9, 2016

xviii) Thomas Heine, Plenary lecture, German Chemistry Association, Unit Solid State Chemistry, Innsbruck, Austria, September 19-22, 2016

xix) Bongkwan Baek, Jae Hyo Han, Dongwon Yoo and Jinwoo Cheon, Chemical Synthesis of Two-Dimensional Transition Metal Chalcogenide Nanostructures, Flatlands Beyond Graphene 2016, Bled, Slovenia, July 5-8, 2016

xx) Jaewon Lee, Wonil Jung, Minji Ahn and Jinwoo Cheon, Synthetic Strategy for Single-Layer Transition-Metal Chalcogenides, Flatlands Beyond Graphene 2016, Bled, Slovenia, July 5-8, 2016

xxi) Jae Hyo Han, Youngsoo Kim, Minkyoung Kwak, and Jinwoo Cheon, Chemically driven surface activations of 2D Layered TMC nanostructures, Poster, Flatlands 2017, EPFL, Lausanne, Switzerland, August 29, 2017

xxii) Bongkwan Baek, Ho Jin, Minji Ahn, Minkyoung Kwak, Youngsoo Kim, Dong Hee Son, and Jinwoo Cheon, Lateral Quantum Confinement effects in single-layer quantum dots of WSe_2, Poster, Flatlands 2017, EPFL, Lausanne, Switzerland, August 29, 2017

*Appendix

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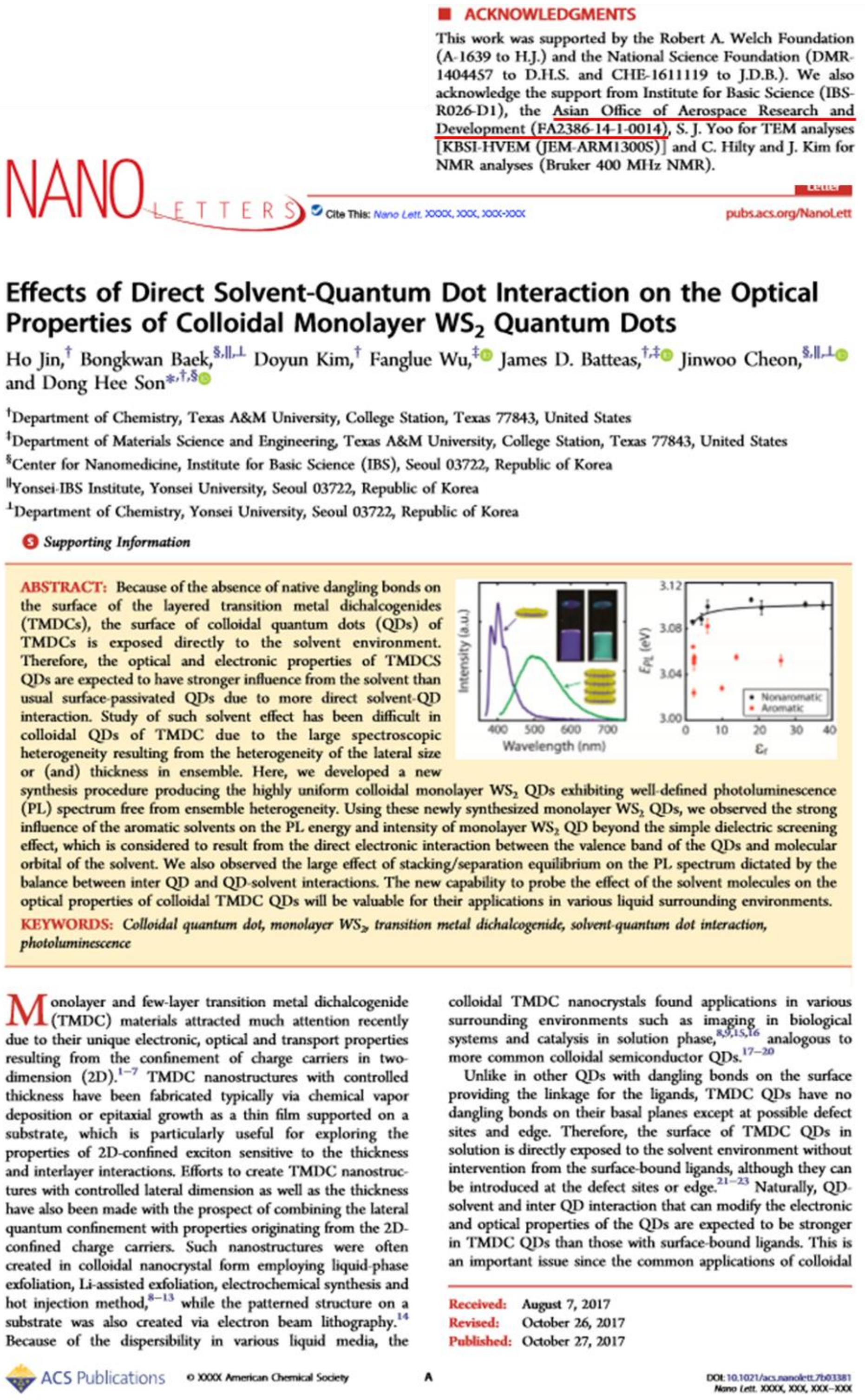

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Letter

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Effects of Direct Solvent-Quantum Dot Interaction on the Optical Properties of Colloidal Monolayer WS_2 Quantum Dots

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Ⓢ *Supporting Information*

ABSTRACT: Because of the absence of native dangling bonds on the surface of the layered transition metal dichalcogenides (TMDCs), the surface of colloidal quantum dots (QDs) of TMDCs is exposed directly to the solvent environment. Therefore, the optical and electronic properties of TMDCS QDs are expected to have stronger influence from the solvent than usual surface-passivated QDs due to more direct solvent-QD interaction. Study of such solvent effect has been difficult in colloidal QDs of TMDC due to the large spectroscopic heterogeneity resulting from the heterogeneity of the lateral size or (and) thickness in ensemble. Here, we developed a new synthesis procedure producing the highly uniform colloidal monolayer WS_2 QDs exhibiting well-defined photoluminescence (PL) spectrum free from ensemble heterogeneity. Using these newly synthesized monolayer WS_2 QDs, we observed the strong influence of the aromatic solvents on the PL energy and intensity of monolayer WS_2 QD beyond the simple dielectric screening effect, which is considered to result from the direct electronic interaction between the valence band of the QDs and molecular orbital of the solvent. We also observed the large effect of stacking/separation equilibrium on the PL spectrum dictated by the balance between inter QD and QD-solvent interactions. The new capability to probe the effect of the solvent molecules on the optical properties of colloidal TMDC QDs will be valuable for their applications in various liquid surrounding environments.

KEYWORDS: *Colloidal quantum dot, monolayer WS_2, transition metal dichalcogenide, solvent-quantum dot interaction, photoluminescence*

Monolayer and few-layer transition metal dichalcogenide (TMDC) materials attracted much attention recently due to their unique electronic, optical and transport properties resulting from the confinement of charge carriers in two-dimension (2D).[1−7] TMDC nanostructures with controlled thickness have been fabricated typically via chemical vapor deposition or epitaxial growth as a thin film supported on a substrate, which is particularly useful for exploring the properties of 2D-confined exciton sensitive to the thickness and interlayer interactions. Efforts to create TMDC nanostructures with controlled lateral dimension as well as the thickness have also been made with the prospect of combining the lateral quantum confinement with properties originating from the 2D-confined charge carriers. Such nanostructures were often created in colloidal nanocrystal form employing liquid-phase exfoliation, Li-assisted exfoliation, electrochemical synthesis and hot injection method,[8−13] while the patterned structure on a substrate was also created via electron beam lithography.[14] Because of the dispersibility in various liquid media, the colloidal TMDC nanocrystals found applications in various surrounding environments such as imaging in biological systems and catalysis in solution phase,[8,9,15,16] analogous to more common colloidal semiconductor QDs.[17−20]

Unlike in other QDs with dangling bonds on the surface providing the linkage for the ligands, TMDC QDs have no dangling bonds on their basal planes except at possible defect sites and edge. Therefore, the surface of TMDC QDs in solution is directly exposed to the solvent environment without intervention from the surface-bound ligands, although they can be introduced at the defect sites or edge.[21−23] Naturally, QD-solvent and inter QD interaction that can modify the electronic and optical properties of the QDs are expected to be stronger in TMDC QDs than those with surface-bound ligands. This is an important issue since the common applications of colloidal

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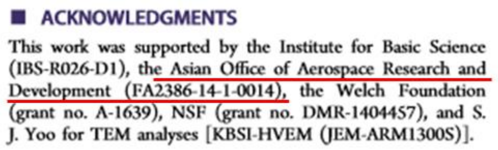

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Colloidal Single-Layer Quantum Dots with Lateral Confinement Effects on 2D Exciton

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Ⓢ *Supporting Information*

ABSTRACT: Controlled lateral quantum confinement in single-layer transition-metal chalcogenides (TMCs) can potentially combine the unique properties of two-dimensional (2D) exciton with the size-tunability of exciton energy, creating the single-layer quantum dots (SQDs) of 2D TMC materials. However, exploring such opportunities has been challenging due to the limited ability to produce well-defined SQDs with sufficiently high quality and size control, in conjunction with the commonly observed inconsistency in the optical properties. Here, we report an effective method to synthesize high-quality and size-controlled SQDs of WSe_2 via multilayer quantum dots (MQDs) precursors, which enables grasping a clear picture of the role of lateral confinement on the optical properties of the 2D exciton. From the single-particle optical spectra and polarization anisotropy of WSe_2 SQDs of varying sizes in addition to their ensemble data, we reveal how the properties of 2D exciton in single-layer TMCs evolve with increasing lateral quantum confinement.

■ INTRODUCTION

In recent years, two-dimensional (2D) transition-metal chalcogenides (TMCs) have emerged as an important class of materials, where the new material properties are obtained by reducing the dimensionality.[1−6] For instance, the band gap of various semiconducting TMCs changes from an indirect to a direct gap with a concomitant appearance of strong exciton photoluminescence (PL) when they become single-layer thick.[7−12] The valley-selective excitation, providing a new degree of freedom to manipulate the material properties, also becomes possible in single-layer TMCs.[13−15] Furthermore, the reduced dimensionality and weaker screening effect can result in the formation of a strongly bound 2D exciton that largely determines the optical and charge transport properties of single-layer TMCs.[16−18] For single-layer TMCs, the reduction of the lateral size to the nanoscale can potentially combine the unique property of the 2D exciton with additional lateral confinement, creating the 'single-layer quantum dot (SQD)' that is distinctly different from more common quantum dots (QDs) derived from 3D crystals. To explore the properties of SQDs to reveal the effect of lateral confinement on 2D excitons in single-layer TMC materials, SQDs should not only satisfy the strict single-layer thickness requirement and lateral size controllability but also maintain single crystallinity without defects. However, there have been synthetic challenges to meet such criteria simultaneously. Some of the commonly employed methods utilize multistep exfoliation of the bulk TMCs to create SQDs.[19−22]

Since these methods typically require intense sonication and/or the use of highly reactive chemicals, such as Li^+, the resulting products tend to suffer from inhomogeneity of lateral size and/or thickness and difficulty maintaining single crystallinity without structural deformations. For example, the structural defects produce the trap states, such as vacancy or deformation of the crystal structure, which are known to form during the harsh exfoliation processes and can interfere with the characterization of the properties of the exciton, as in the case for common colloidal QDs. Therefore, despite the observation that the size-dependent PL suggests a possible lateral confinement effect,[19−24] understanding of the properties of 2D exciton in single-layer TMCs experiencing lateral quantum confinement has remained elusive.

In this study, we report a highly effective method to have high-quality, lateral size-controlled SQDs of TMCs with a circular shape using multilayer quantum dots (MQDs) as the precursor. The method involves the initial synthesis of disc-shaped MQDs with a controlled diameter followed by mild exfoliation via tandem molecular intercalation (TMI), producing SQDs that inherit the diameter and crystal phase of the initial MQDs without creating defects[25] (Scheme 1).

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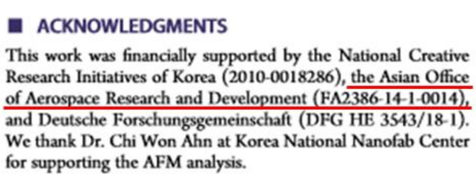

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Colloidal Synthesis of Single-Layer MSe_2 (M = Mo, W) Nanosheets via Anisotropic Solution-Phase Growth Approach

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Supporting Information

ABSTRACT: The generation of single-layer 2-dimensional (2D) nanosheets has been challenging, especially in solution-phase, since it requires highly anisotropic growth processes that exclusively promote planar directionality during nanocrystal formation. In this study, we discovered that such selective growth pathways can be achieved by modulating the binding affinities of coordinating capping ligands to the edge facets of 2D layered transition-metal chalcogenides (TMCs). Upon changing the functional groups of the capping ligands from carboxylic acid to alcohol and amine with accordingly modulated binding affinities to the edges, the number of layers of nanosheets is controlled. Single-layer MSe_2 (M = Mo, W) TMC nanosheets are obtained with the use of oleic acid, while multilayer nanosheets are formed with relatively strong binding ligands such as oleyl alcohol and oleylamine. With the choice of appropriate capping ligands in the 2D anisotropic growth regime, our solution-based synthetic method can serve a new guideline for obtaining single-layer TMC nanosheets.

Recently, single-layer sheets of van der Waals (vdW) transition-metal chalcogenides (TMCs), in which single layers are held together by vdW force,[1] have emerged as uniquely important nanostructures with unprecedented materials properties, analogous to graphene.[2] These single-layer TMCs exhibit remarkable materials characteristics when compared to their multilayer bulk counterpart. For example, when group VI TMC nanomaterials become thinned to the single layer, the electronic structure of indirect band gap in the bulk changes to direct band gap with enhanced optoelectronic transitions.[3] In addition, the excellent in-plane charge carrier mobility and giant spin-valley coupling are some of the electronic characteristics that can enable the high-performance capabilities of optoelectronic and spintronic devices.[4]

During the past decade, solution methods have been demonstrated as one of the most powerful synthetic approaches for a wide range of nanostructures composed of covalent-networks between metals and chalcogens,[5] including 0-dimensional (0D) quantum dots, 1-dimensional (1D) nanowires, and 2-dimensional (2D) nanosheets.[6] For example, CdSe nanocrystals have been successfully synthesized in a size- and shape-controlled fashion from spheres[6a,b] to platelets[6e,f] and branched complex structures.[6d] Even with such synthetic advances, one of the current challenges is the lack of proper synthetic protocols for free-standing single-layer 2D nanosheets of vdW TMCs.[7] According to the recent studies, even though solution-based synthetic methods have provided some glimpse on the formation of single-layer TMCs in the early stage of growth processes,[8] multilayered TMCs are typically isolated as stable products.[9] One most recent study shows that controlled delivery of chalcogen source during the crystal growth processes is critical to generate single layers of group IV TMCs such as TiS_2, ZrS_2, and HfS_2.[10] Even with these studies, the understanding and the control of growth processes for single-layer TMC nanosheets are still elusive, not to mention the lack of reliable synthetic protocols.

In this study, we demonstrate a colloidal methodology for single-layer nanosheets of MSe_2 (M = Mo, W) by exclusively promoting their anisotropic lateral growth mode. We discovered that the use of specific surface capping ligands with different binding energies to the reactive edge facets of TMCs is the most important factor to produce thickness-controlled TMCs from multi- to single-layer. The strength of ligand binding to the given crystallographic facet is theoretically examined to understand the ligand-dependent anisotropic growth modes. While the roles of capping ligands on the anisotropic growth effects for other 0D and 1D nanostructures are well-known, this is the first demonstration of capping ligand-driven synthetic protocol for single-layer nanosheets of vdW TMCs.

As a representative case of our study, we first chose WSe_2. Each layer of WSe_2 is weakly bonded by vdW force and comprises a Se−W−Se triatomic layer where tungsten (W) is covalently bonded to six selenium (Se) atoms in a trigonal prismatic geometry (Figure 1a).[11] WSe_2 nanosheets are synthesized by reacting tungsten hexacarbonyl ($W(CO)_6$) and diphenyl diselenide (Ph_2Se_2) in the presence of capping ligand as a solvent (Figure 1b).[12] We tested three different types of capping ligands (i.e., oleylamine, oleyl alcohol, and oleic acid) having the same number of carbon atoms, but different terminal functional groups. $W(CO)_6$ (0.02 mmol) is reacted with Ph_2Se_2 (0.04 mmol) in the excess amount of capping ligand (14 mmol) at 330 °C under an Ar atmosphere. After 12 h, the reaction mixture is cooled down and centrifuged to isolate WSe_2 nanosheets with high colloidal stability when dispersed in nonpolar solvents such as toluene (Figure S2). According to our DFT calculations, such

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Nanoflakes **Hot Paper**

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Hexagonal Transition-Metal Chalcogenide Nanoflakes with Pronounced Lateral Quantum Confinement**

Pere Miró, Jae Hyo Han, Jinwoo Cheon, and Thomas Heine**

Dedicated to Professor Gerhard Roewer on the occasion of his 75th birthday

Abstract: *Transition-metal chalcogenide (TMC) nanoflakes of composition MX_2 (where M = Ti, Zr and Hf; X = S and Se) crystallize preferentially in equilateral hexagons and exhibit a pronounced lateral quantum confinement. The hexagonal shape of octahedral (1T) TMC nanoflakes is the result of charge localization at the edges/vertices and the resulting Coulomb repulsion. Independent of their size, all nanoflakes have the M_nX_{2n-2} stoichiometry and thus an unoxidized metal center which results in dopant states. These states become relevant for small nanoflakes and lead to metallic character, but for larger nanoflakes (> 6 nm) the 2D monolayer properties dominate. Finally, coordination of Lewis bases at the nanoflake edges has no significant effect on the electronic structure of these species confirming the viability of colloidal synthetic approaches.*

The existence of two dimensional (2D) materials was a highly debated issue in solid-state physics concluding that these materials would be thermodynamically unstable at any finite temperature owing to thermal fluctuations.[1,2] The scientific community had to wait until last decade to disprove these statements and exfoliate graphite to graphene, the first 2D material to be isolated.[3,4] After this major scientific breakthrough, other layered materials, such as hexagonal boron nitride (*h*-BN), and transition-metal chalcogenides (TMCs) have been exfoliated down to monolayers.[5–7] Nowadays, 2D materials are a rapidly growing multidisciplinary field with a wide range of applications in nano- and optoelectronics, catalysis, and energy storage.[8] Transition-metal dichalcogenides are a prominent family of layered materials with the general formula of MX_2, where M is a transition metal and X is a chalcogen element. These materials are composed of 2D sheets stacked on top of one another. Each sheet is three atoms thick, with metal atoms in the middle, each of them covalently bound to the chalcogen atoms located above and below (Figure 1 a). In the bulk and in stacked aggregates, TMC sheets are held together through interlayer London dispersion interactions. Nanostructures of layered TMCs are highly promising owing to their unique chemical and physical properties derived from the different nature of intra- and interlayer bonding. This provides a wide range of interesting anisotropic features for ion intercalation, spintronics, optoelectronics, and catalysis.[9–14] Furthermore, fascinating properties emerge when either the number of layers or the lateral system size is changed. For example, the exfoliation of bulk MoS_2 leads to photoluminescence at the monolayer level, while lateral confinement in WS_2 nanoflakes enhances its luminescence efficiency.[15–18] In this respect, the recent advances in the growth of TMC nanocrystals with a bottom-up synthetic approach have provided a route

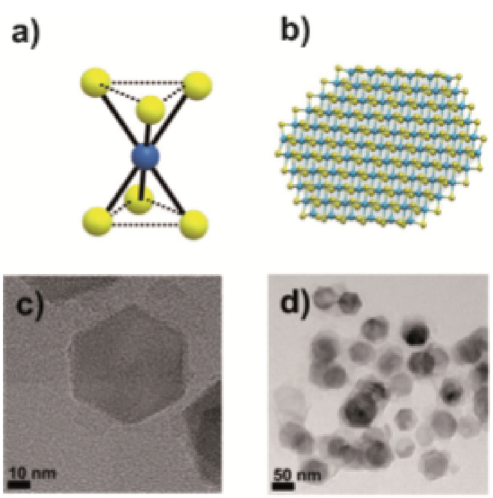

Figure 1. a) Visualization of basic atomic coordination of 1T-MX_2. b) atomic ball model of hexagonal shaped 2D transition-metal dichalcogenide nanoflake model with chemical composition of $Ti_{37}S_{72}$ (Ti_{37}^{hex}) employed in this study. c) High- and d) low-magnification TEM images of synthesized hexagonal shaped TiS_2 nanoflakes. Transition metals blue, chalcogens yellow.

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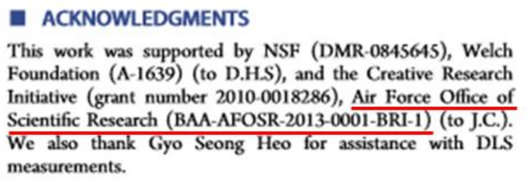

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Photoinduced Separation of Strongly Interacting 2-D Layered TiS_2 Nanodiscs in Solution

Daniel Rossi,[†] Jae Hyo Han,[‡] Dongwon Yoo,[‡] Yitong Dong,[†] Yerok Park,[†] Jinwoo Cheon,*[‡] and Dong Hee Son*[†]

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Ⓢ *Supporting Information*

ABSTRACT: Colloidal 2-D layered transition metal dichalcogenide (TMDC) nanodiscs synthesized with uniform diameter and thickness can readily form the vertically stacked assemblies of particles in solution due to strong interparticle cohesive energy. The interparticle electronic coupling that modifies their optical and electronic properties poses a significant challenge in exploring their unique properties influenced by the anisotropic quantum confinement in different directions taking advantage of the controlled diameter and thickness. Here, we show that the assemblies of 2-D layered TiS_2 nanodiscs are efficiently separated into individual nanodiscs via photoexcitation of the charge carriers by pulsed laser light, enabling the characterization of the properties of noninteracting TiS_2 nanodiscs. Photoinduced separation of the nanodiscs is considered to occur via transient weakening of the interparticle cohesive force by the dense photoexcited charge carriers, which facilitates the solvation of each nanodisc by the solvent molecules.

INTRODUCTION

Atomically thin 2-D layered transition metal dichalcogenide (TMDC) nanostructures are attracting much attention due to their material properties that are sensitive to the number of layers and the strength of their interlayer interaction.[1−4] Often these materials are synthesized via exfoliation from bulk or using chemical vapor deposition (CVD) methods, which produce single and few-layer thin flakes enabling detailed studies of the thickness-dependent material properties of TMDC.[1,5−7] Recently, solution-phase synthesis methods have been developed for several TMDC materials, enabling the production of uniform ensembles of colloidal TMDC nanodiscs with simultaneously controlled thickness and lateral area.[8] Colloidal 2-D layered TMDC nanodiscs with controllable thickness and area provide a unique opportunity to explore the material properties correlated with both variation of interlayer interaction and intralayer spatial confinement that are expected to be highly anisotropic.[1]

Optical absorption has frequently been used to correlate the electronic structure with the dimensions or morphology of the colloidal nanoparticles, provided that the size and shape distributions are narrow and that the particles are well separated within the solution.[9,10] In typical colloidal solutions of inorganic nanoparticles, surface-bound ligands or surface ions provide the colloidal stability, keeping the particles separated from each other. Ordered assemblies or aggregates of the interacting particles can also form within the solution depending on the factors that determine the balance between interparticle cohesive energy and particle solvation, such as surface passivation, solvent polarity, etc. Interparticle interactions and the formation of the assemblies of interacting particles is an important issue since the electronic, optical, and transport properties of the particles can change significantly via electronic coupling.[11−15] Colloidal 2-D layered TMDC nanodiscs have large flat basal planes, and the possible interparticle contact area that affects interparticle cohesive energy and electronic coupling is much larger than that in 0-D and 1-D structures of the same volume. Therefore, the formation of an interacting assembly of particles is more facile than that in 0-D and 1-D structures, and its effect on the optical and electronic properties can also be more significant.[16,17] The alteration of the optical properties due to interparticle electronic coupling can pose a challenge in exploring the unique dimensionally anisotropic properties of transition metal dichalcogenide nanostructures using colloidal nanoparticles with well-controlled lateral and transverse dimensions.

In this study, we show that the vertically stacked assemblies of TiS_2 nanodiscs present in the colloidal solution due to the strong interparticle interaction via basal planes can be readily separated into individual noninteracting nanodiscs via pulsed photoexcitation. Interband photoexcitation of TiS_2 nanodiscs with pulsed laser light creates dense charge carriers that transiently modify the charge distribution within the nanodiscs. The change in charge distribution in TiS_2 nanodiscs during the lifetime of the charge carriers is considered to nonthermally weaken the interparticle cohesive energy and facilitate the

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