Poster Presentation : (발표세션을 적어주세요.)

2021년도 한국현미경학회

춘계학술대회

Controllable Synthesis of Platinum Diselenide Inorganic Fullerene

Seung Min Yu[1], Mengjing Wang[2], Mashiyat Sumaiya Shawkat[2], Zheng Xi[3], Sang-Sub Han[4], Xiaohu Xia[3],Gyu-Hwan Oh[4], Kyu Seung Lee[5], Dong Ick Son[5], Tae-Sung Bae[1], Hyeon Ih Ryu[1], Hee-Suk Chung[1], Yeonwoong Jung[2]

[1]Korea Basic Science Institute, Jeonju, Jeonbuk, Republic of Korea, 54907

[2]NanoScience Technology Center, University of Central Florida, Orlando, FL32826, USA

[3]Department of Chemistry, University of Central Florida, Orlando, FL32826, USA

[4]Department of Materials Science and Engineering, Seoul National University, Republic of Korea

[5]Institute of Advanced Composite Materials, Korea Institute of Science and Technology, Jeonbuk 55324, Republic of Korea

발표자 : 유승민, 정희석

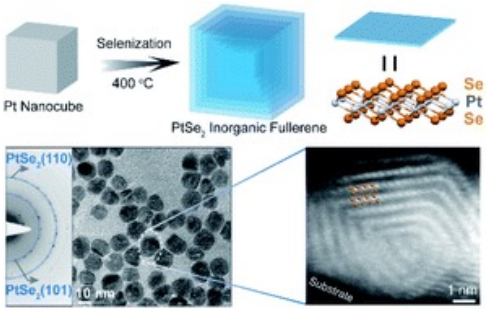
한국기초과학지원연구원

hschung13@kbsi.re.kr

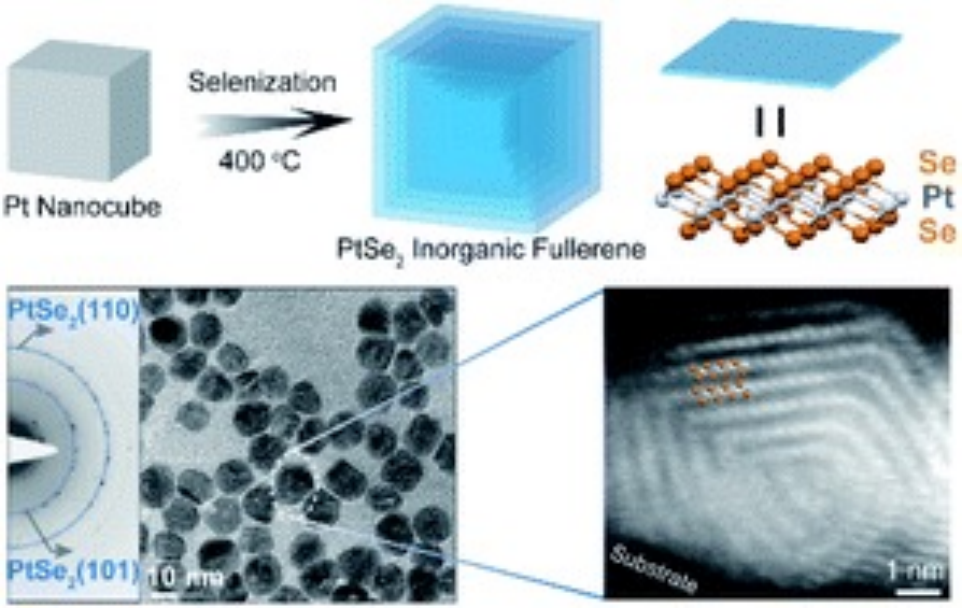
한국현미경학회

Korean Society of Microscopy

Layered transition metal dichalcogenide (TMD) crystals in reduced dimensions have exhibited a wide range of extraordinary physical and chemical properties spanning from exotic quantum phenomenon to unusually superior chemical reactivity. Their anisotropic van der Waals (vdW) bonding nature enables them to commonly possess two-dimensional (2D) structures which have been rigorously investigated recently. Nonetheless, TMD crystals in quasi zero-dimensional (0D) forms, i.e., TMD fullerenes, have not been explored in depth from the perspective of reproducible synthesis and process-structure correlation. Herein, we report a controlled synthesis of inorganic fullerene platinum diselenide (PtSe2) via a thermal selenization of Pt nanostructured precursors. We identified a conversion of Pt nanocubes to PtSe2 “onion-like” fullerenes, dictated by a well-defined isotropic volume expansion. Extensive transmission electron microscopy (TEM) inspections revealed that there exists a certain size-dependency which leads to the preferable growth of PtSe2 fullerenes over 2D PtSe2 platelets. The underlying principle for this size-dependent growth is discussed in the context of surface energy minimization. Furthermore, the PtSe2 fullerenes were verified to possess a large degree of unsaturated dangling bonds as well as internal strain, verified by Raman and X-ray photoelectron spectroscopy (XPS) spectroscopies as well as a geometric phase analysis (GPA). This study sheds light on synthesizing a wide range of TMD-based fullerenes which will foster the discovery of novel physical and chemical properties in quasi 0D material systems.



Herein, we report a morphology-controlled synthesis of quasi-0D fullerenes composed of $PtSe_2$ – a representative example of Pt-based TMDs. Pt nanoparticles of distinct shapes were converted to vdW-$PtSe_2$ nanostructures through a thermal selenization at 400 °C. It was identified that $PtSe_2$ fullerenes were only produced from Pt nanoparticles that satisfied a certain criterion of size and geometrical factor. Selenizing Pt nanocubes of near isotropic shape and uniform sizes yielded homogeneous quasi-0D $PtSe_2$ fullerenes by retaining the theoretically-predicted volume expansion. Otherwise, their 2D counterparts of 1T-phased $PtSe_2$ nanoplatelets were preferably formed. This selection rule is discussed in the context of the total energy minimization associated with the conversion of Pt to $PtSe_2$. A series of TEM analysis confirmed that the $PtSe_2$ fullerenes possess “onion-like” nested structures manifested by multi-layered outer shells with hollow or solid inner cores. Furthermore, the $PtSe_2$ fullerenes were observed to contain a large degree of unsaturated dangling bonds and vdW gaps, as verified by Raman and XPS spectroscopy characterization. These unique structural attributes, combined with their enriched internal strain identified by a GPA method, suggest their high promise for electrochemically-driven catalytic and sensing applications.



Preparation of Pt nanocubes: 40 mg polyvinylpyrrolidone (PVP, $M_w \approx 55\,000$) and 20 mg potassium bromide (KBr) were first dissolved in 3 mL ethylene glycol (EG) solution hosted in a 20 mL vial and preheated to 180 °C in an oil bath under magnetic stirring for 10 min. Then 20 mg $Na_2PtCl_6 \cdot 6H_2O$ dissolved in 1 mL EG was quickly pipetted into the vial. The reaction was allowed to proceed for 20 min and then cooled down to room temperature. The Pt nanocubes as products were then washed once with acetone and twice with deionized water, collected by centrifugation and finally dispersed in deionized water for further use. As-synthesized Pt nanocubes were drop casted on the fused silica substrate or silicon nitride TEM grid and dried overnight before selenization.

Preparation of annealed Pt films: Pt film of ~0.5 nm thickness was deposited onto sapphire substrates or silicon nitride membranes by an electron beam evaporator (Thermionics VE-100) at a fixed evaporation rate of 0.15 Å/s. The Pt-deposited substrates were placed in the center zone of a quartz tube in a thermal furnace (Lindberg/Blue M Mini-Mite). Subsequently, it was purged with Ar gas three times, achieving a base pressure of ~ 1 mTorr followed by annealing at 900 °C for 30 mins with a ramp rate of 10 °C/min. The entire annealing was performed under a constant Ar flow of ~100 SCCM, which leads to the operation pressure of ~ 75 mTorr.

Growth of $PtSe_2$ fullerenes and platelets: The substrates covered with Pt nanocubes or annealed Pt films were placed in the center of the thermal furnace with an alumina boat containing Se powder in the upstream side. Following the Ar purging (described above), the furnace was heated to the reaction temperature of 400 °C at a ramp rate of ~7 °C/min and was maintained for 50 min. During the reaction, Se was vaporized at 200 °C and was supplied at a pressure of ~75 mTorr by the flow of Ar gas at ~100 SCCM.

Electron microscope characterization and geometric phase analysis: TEM imaging and tilting experiment of $PtSe_2$ nanoparticles were performed using FEI F30 TEM (operation voltage: 300 kV). STEM imaging of cross-sectional samples was performed using JEOL ARM 200F Cs-corrected TEM (operation voltage: 200 kV). Cross-sectional TEM/STEM samples were prepared by focused ion beam (FIB; Quanta 2D FEG, FEI)-based milling and lift-out techniques using gallium (Ga) ion beam (30 keV) and a micromanipulator (Omniprobe) inside the FIB. The geometrical phase analysis (GPA) of HAADF-STEM images was performed using an open source program Strain++ (https://jjppeters.github.io/Strainpp).

Raman and XPS characterization: Raman spsectroscopy combined with a scanning electron microscopy was utilized with a solid-state laser system (WITec) at the excitation wavelength of 532nm. XPS characterization was carried out using Thermo VG Scientific K-α system with an Al Kα ray source under ultrahigh vacuum conditions.

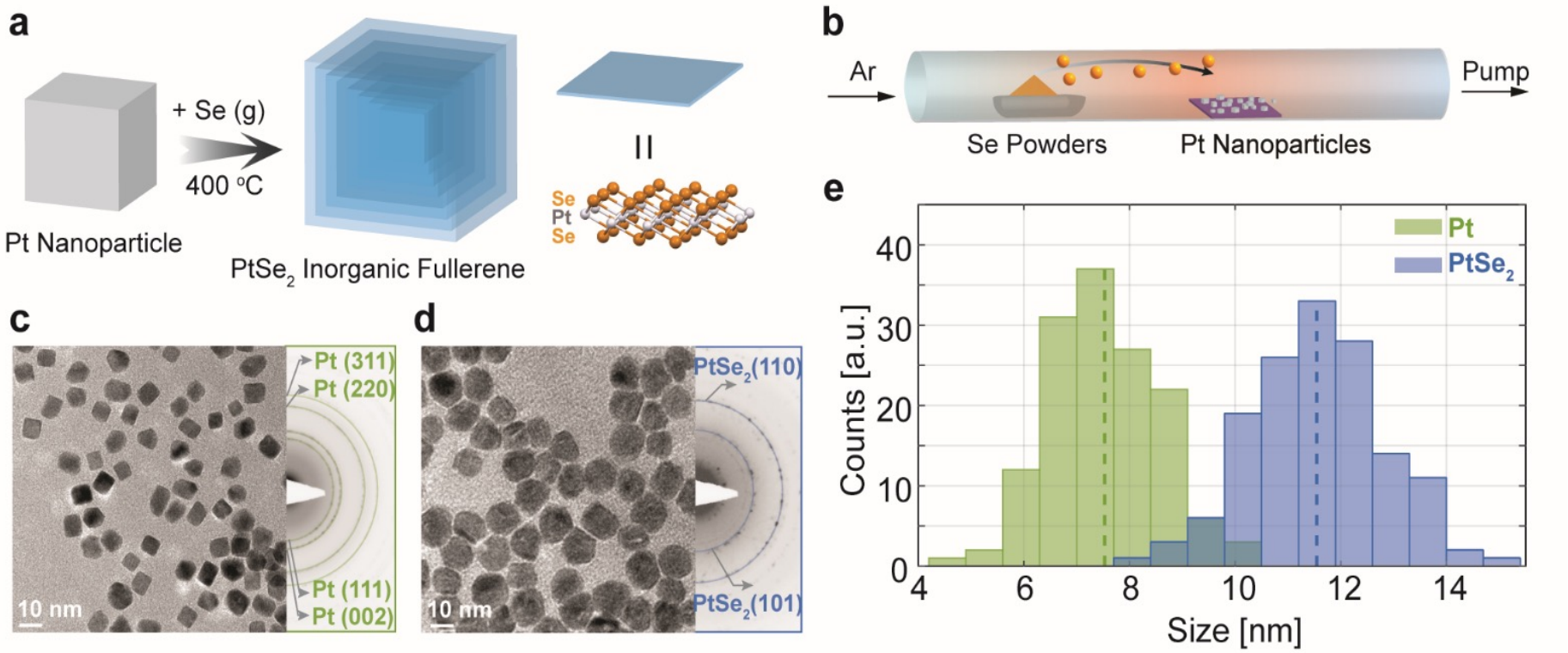


Fig. 1 (a) Schematic of morphology transformation from Pt nanocube (grey) to $PtSe_2$ fullerene (blue). Each blue plane in the fullerene corresponds to a single layer of 1T-$PtSe_2$. (b) Schematic of the experimental setup for the controlled selenziation of Pt nanocubes to grow $PtSe_2$ fullerenes. (c-d) Mid-resolution TEM (left) and SAED (right) characterizations of initial Pt nanocubes and resulting $PtSe_2$ fullerenes, respectively. (e) Size distribution histogram of Pt nanocubes and $PtSe_2$ fullerenes determined from (c) and (d). Green and blue dashed lines mark the average size for each distribution.

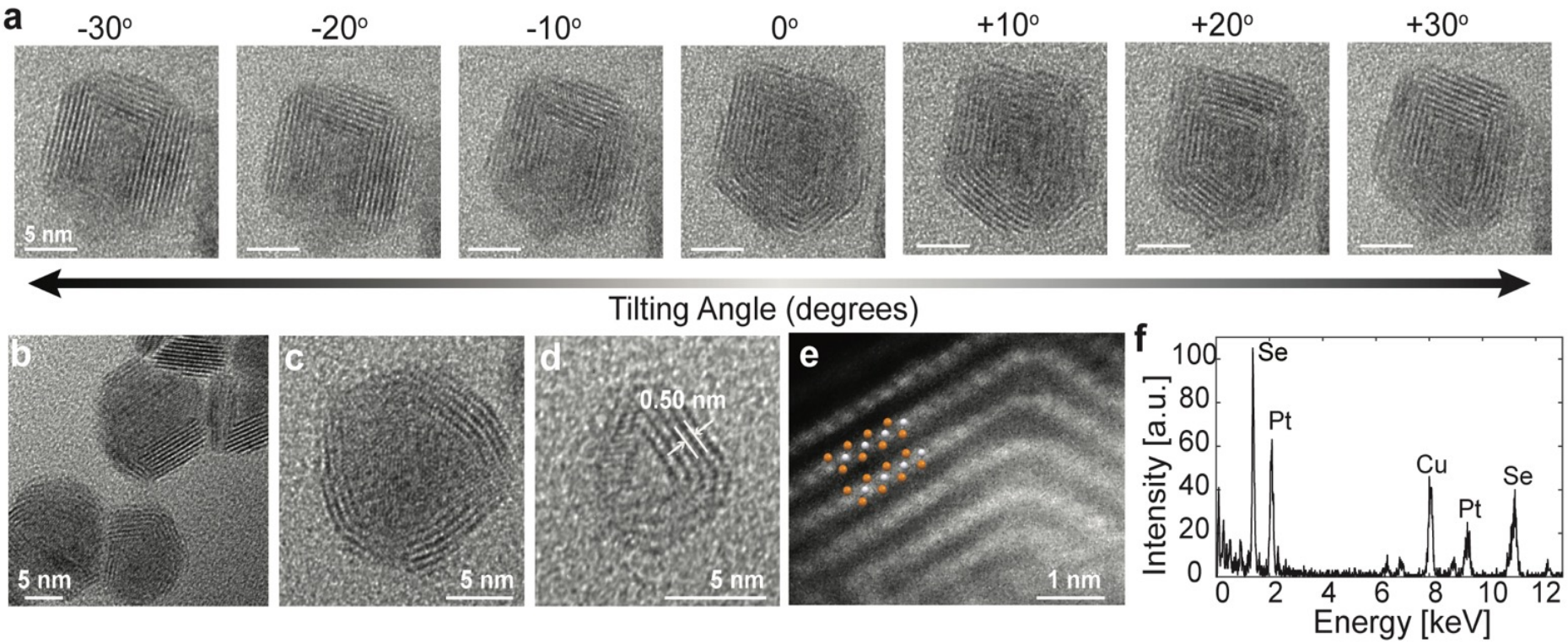


Fig. 2 (a) Representative HRTEM images of a $PtSe_2$ fullerene obtained at various TEM stage tilting angles from -30° to +30° along a fixed vertical axis. (b) HRTEM image of multiple $PtSe_2$ fullerenes obtained by the selenization of Pt nanocubes. (c-d) HRTEM images of $PtSe_2$ fullerenes with hollow (c) and solid (d) cores. (e) Cross-sectional STEM image of a $PtSe_2$ fullerene with an overlay of Pt (grey) and Se (orange) atoms arranged in 1T configuration. (f) EDS characterization of $PtSe_2$ fullerenes. Cu signal comes from the TEM grids.

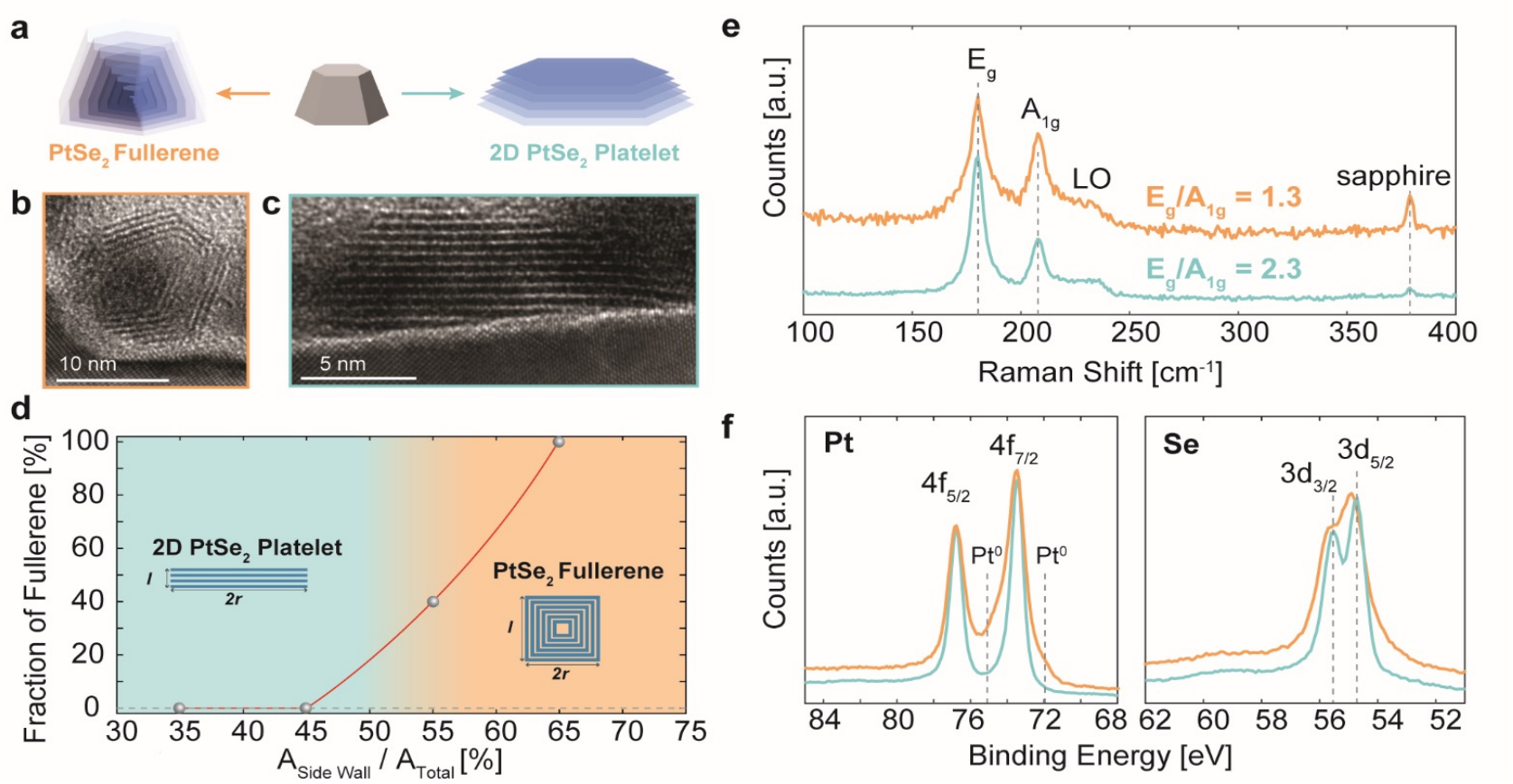


Fig. 3 (a) Schematic of morphology transformation from annealed Pt film (nearly-hexagonal Pt domains, grey) towards $PtSe_2$ fullerene (blue) and 2D $PtSe_2$ platelet (blue). Cross-sectional TEM characterization of (b) a $PtSe_2$ fullerene, and (c) a 1T-$PtSe_2$ platelet grown on a sapphire substrate. (d) Fraction of $PtSe_2$ fullerenes as a function of ratio of side wall area over total surface area. Insets are schematics of cross-section of 2D-platelet and quasi- 0D- fullerene with lateral size (2r) and vertical height (l) marked. (e) Raman spectra of $PtSe_2$ fullerenes (orange line, top) and 1T-$PtSe_2$ platelets (green line, bottom). (f) XPS spectra of $PtSe_2$ fullerenes (orange line, top) and 1T-$PtSe_2$ platelets (green line, bottom).

We hypothesize that a $PtSe_2$ nanostructure at its initial growth stage assumes a quasi-cylindrical shape with r being the radius and l being the vertical height. The variation of these dimensional parameters determines its final geometry after full growth. Akin to the growth of 1D semiconductor nanowires[42, 43], the total energy (E_{tot}) of a $PtSe_2$ nanostructure during its initial growth accounts for the energy contributions from all constituting faces, including side ($A_{side} \cdot \gamma_{side}$) and top ($A_{top} \cdot \gamma_{top}$) faces as well as the $PtSe_2$-substrate interface ($A_{bottom} \cdot \gamma_{interface}$) energies. Here, A and γ denote the area and the surface/interface energy of a constituting face, respectively; i.e., $A_{top} = A_{bottom} = \pi r^2$, $A_{side} = 2\pi rl$. Assuming the cylindrical geometry, E_{tot} can be expressed as:

$$E_{tot} = 2\pi rl \cdot \gamma_{side} + \pi r^2 \cdot \gamma_{top} + \pi r^2 \cdot \gamma_{interface}$$

The interfacial energy ($\gamma_{interface}$) of $PtSe_2$-substrate can be neglected with respect to the other energy contributions (γ_{side}, γ_{top}) as it presents a solid-solid interface whose energy value is known to be much smaller than those of solid-vacuum interfaces[42]. In TMDs, the edges of their constituting 2D layers possess a significantly higher density of dangling bonds than the basal planes, thus their formation is less thermodynamically favored due to the higher surface energy[44]. As a result, the total surface energy contribution in equation (1) is determined by the relative competition of constituting faces - i.e., the ratio of A_{side} and A_{total}. We correlate the fraction of observing $PtSe_2$ fullerenes vs. A_{side}/A_{total} inspected from a large number of cross-sectional TEM data and present the correlation plot in Fig. 3d. The boundary between the 2D platelet (green) vs. the quasi 0D-fullerene (orange) regimes indicates that the geometric factor of A_{side}/A_{total} plays an essential role in determining preferred growth characteristics. With increasing A_{side}/A_{total}, i.e., increasing l/r, the growth of fullerene structures is thermodynamically more favored over 2D platelets. For instance, selenizing Pt nanocubes of A_{side}/A_{total} ~ 0.67 produces $PtSe_2$ fullerenes with nearly 100 % yield. This observation indicates that the energy contribution from the “side” faces becomes more pronounced with increasing A_{side}/A_{total}. Accordingly, $PtSe_2$ nanostructures prefer to grow exposing crystalline planes of a smaller surface energy – i.e. basal planes – on the side faces, resulting in the growth of fullerenes. Meanwhile, when $A_{side}/A_{total} \sim l/r$ is small, the energy contribution from the side faces becomes insignificant and the total energy is dominated by the surface energy of “top” faces. This case will favor the growth of vertically-stacked basal planes in a layer-by-layer manner by exposing their edges on the side faces

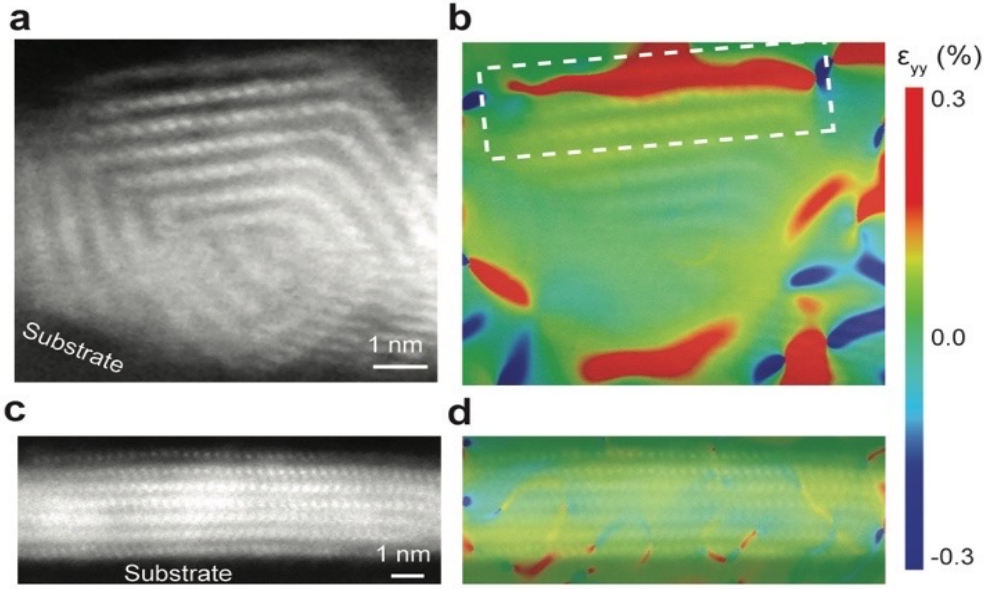


Fig. 4 STEM and GPA strain mapping images of $PtSe_2$ fullerene (a,b) and platelet (c,d). The white dashed box in (b) highlights the distribution of tensile strain accumulated along the edge of the fullerene.

We report a new solid-gas reaction method for the controlled synthesis of quasi-0D $PtSe_2$ fullerenes. The synthesis is based on the thermal selenization of Pt nanocubes, which yields fullerenes of well-defined dimension, morphology, and size ratios. Comprehensive TEM investigations reveal that the surface energy contribution associated with the thermal conversion of Pt to $PtSe_2$ plays a critical role in determining the final growth morphology. Raman and XPS characterization indicate that $PtSe_2$ fullerenes expose a larger degree of vdW gaps and layer edges compared to their 2D counterpart platelets. GPA strain map analysis also confirms that the fullerenes assume a substantial amount of tensile strain along their peripheral shells. This synthesis methodology provides guidelines to produce a wide array of quasi-0D TMD crystals in a controllable manner, paving the path for experimentally exploring their projected superior catalytic performances and novel physical phenomena.

** This work was supported by the Technology Innovation Program (20010542, Development of Petroleum Pitch based Conductive Material and Binder for Lithium Ion Secondary Battery and Their Application) funded by the MOTIE, Korea.*

2021 한국현미경학회 춘계학술대회

한국현미경학회
Korean Society of Microscopy