Visualizing Point Defects in Transition-Metal Dichalcogenides Using Optical Microscopy

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ABSTRACT: While transmission electron microscopy and scanning tunneling microscopy reveal atomic structures of point defect and grain boundary in monolayer transition-metal dichalcogenides (TMDs), information on point defect distribution in macroscale is still not available. Herein, we visualize the point defect distribution of monolayer TMDs using dark-field optical microscopy. This was realized by anchoring silver nanoparticles on defect sites of MoS₂ under light illumination. The optical images clearly revealed that the point defect distribution varies with light power and exposure time. The number of silver nanoparticles increased initially and reached a plateau in response to light power or exposure time. The size of silver nanoparticles was a few hundred nanometers in the plateau region as observed using optical microscopy. The measured defect density in macroscale was ∼2 × 10¹⁰ cm⁻², slightly lower than the observed value (4 × 10¹¹ cm⁻²) from scanning tunneling microscopy.

KEYWORDS: molybdenum disulfide, point defect distribution, dark-field optical microscopy, light illumination, Ag nanoparticle

The ability to convert indirect bandgap of multilayer transition-metal dichalcogenides (TMDs) to direct bandgap of monolayer TMDs and existence of various bandgaps in a series of TMDs are great advantages over bulk Si and thus open a new possibility to utilize TMDs for transparent, flexible, and stretchable optoelectronic devices. Nevertheless, the studies are mostly limited to micron-sized flakes that are typically obtained by mechanical exfoliation. Recently, it has been possible to obtain large-area TMDs. For example, monolayer MoS₂ and WS₂ were grown to a large area by chemical vapor deposition (CVD), demonstrating the possibility to integrate layered structures. However, control of structural defects is still limited. Structural defects including grain boundaries and point defects have a significant influence on electrical transport and thermal properties. Therefore, a systematic approach is required for analyzing such defects.

Information on the atomic rearrangement at grain boundaries or vacancies can be obtained using transmission electron microscopy (TEM) or scanning tunneling microscopy (STM). However, information on the distribution of such defects in macroscale is not easily accessible, although electrical transport and thermal properties are easily affected by such macroscopic defect distribution. For example, the sheet resistance of graphene is inversely proportional to its grain size, following a scaling law. Optical approaches including second harmonic generation (SHG) and liquid crystal have been introduced to visualize grain boundaries on CVD-grown MoS₂. Although these methods are noninvasive, sophisticated optical systems are required. In addition, modification of sample surface morphologies by selective oxidation and decoration with metal nanoparticles on defect sites makes it feasible to observe line defects (grain boundaries, wrinkles, and cracks). Furthermore, these approaches are not suitable for observing point defects. Although point defects of TMDs have been observed by decoration with metal nanoparticles on defect sites of MoS₂ using atomic force microscopy (AFM), field-emission scanning electron microscopy (FESEM), and TEM, which are still limited to atomistic information, visualizing macroscopic point-defect distribution has not been achieved to date.

In this article, we visualize point defects as well as grain boundary distributions on CVD-grown TMDs using dark-field optical microscopy. Visualization was achieved by selectively decorating with metal nanoparticles on defect sites.
anchoring Ag nanoparticles on defect sites of TMDs, which were generated by annealing the TiO$_2$/Ag film and aggregated on defect sites of TMDs under white light illumination. While Ag nanoparticles are formed and diffused out through TiO$_2$ during annealing, Ag nanoparticles are photoexcited by localized surface plasmon resonance under light illumination, transferring electrons to TiO$_2$ and dissolving into Ag$^+$ ions, as reported previously. The generated Ag$^+$ ions are reduced and redeposited on defect sites of TMDs. As the light power increased or exposure time was prolonged, the number of Ag nanoparticles increased rapidly initially and reached a constant value at a later stage. The population of Ag nanoparticles deposited on TMDs also relied on the incident light wavelength. The defect density was obtained at the plateau region by counting the number of Ag nanoparticles in a given area that was averaged over the entire region of interest. The estimated defect density on CVD-grown monolayer MoS$_2$ was around 2 × 10$^{10}$ cm$^{-2}$, which is slightly less than the value obtained from STM. This approach using dark-field optical microscopy is applicable to a wide range of TMDs for observing macroscale point-defect distribution.

RESULTS AND DISCUSSION

Figure 1a is the dark-field optical image of CVD-grown monolayer MoS$_2$ transferred onto the TiO$_2$/Ag substrate. Sol-gel prepared TiO$_2$ layer was spin-coated on Ag film deposited by thermal evaporator. Large-area (2 × 2 cm$^2$) monolayer MoS$_2$ grown on SiO$_2$/Si substrate by CVD was coated with poly(methyl methacrylate) (PMMA), floated in deionized water, and then simply fished on the prepared TiO$_2$/Ag film. The sample was dried for 20 min under 60 mW white light illumination. This preparation process is briefly illustrated in Supporting Information (SI), Figure S1. The light spot area was 4 cm in diameter. The optical image of MoS$_2$ on SiO$_2$/Si substrate (left inset of Figure 1a) shows a portion of large-area monolayer MoS$_2$ focusing on the empty region in pink. Several remarkable features are shown in Figure 1a: (i) bright spots like the milky way, indicating the presence of point defects, are clearly visible and uniformly distributed over the entire area; (ii) grain boundary lines are clearly visible; (iii) multilayer portions are distinct from monolayer portions; and (iv) edges are also identified at the empty region of MoS$_2$. The magnified optical images and FESEM morphological images indicate that the bright spots were Ag nanoparticles or their aggregates with sizes of several hundred nanometers (see SI, Figure S2), where the presence of Ag element was confirmed by energy-dispersive X-ray spectroscopy (EDX) mapping (see SI, Figure S3). Ag nanoparticles generated during the sample preparation process (will be discussed later) are anchored preferably at the defect sites such as point defects, grain boundary lines, and edges. Such remarkable visualization of point defects was not clearly obtained in the bright-field image (right inset in Figure 1a). Dark-field image of MoS$_2$ on SiO$_2$/Si substrate (see SI, Figure S4) revealed clear edges at the empty region of MoS$_2$, but no obvious point defects were visible, similar to the aforementioned bright-field image. This clear distinction originates from the enhanced light scattering at the defect sites in dark-field optics. This concept of observation can be generalized to other TMD materials. Monolayer WS$_2$ and WSe$_2$ flakes grown using similar CVD methods with different sources (see the Methods section) were identified by Raman spectra (see SI, Figure S5). The point defects and grain boundaries were revealed to be similar to those of monolayer MoS$_2$ flakes (Figure 1b–d). Further study is needed to investigate the presence of lesser point defects in WSe$_2$ flakes than in other TMD flakes.
The effect of white light power on the defect visualization was investigated and shown in Figure 2. The exposure time was set to be 20 min to ensure that the defect density reaches plateau at a given power (see SI, Figure S6). At a low power of 0.1 mW, only point defects were observed. No Ag nanoparticles were observed within the yellow region (no MoS$_2$ layer), indicating a preferable adsorption of Ag nanoparticles at defect sites of MoS$_2$. At the low power region, the defect density increased in proportion to the light power, and the size of Ag nanoparticles was reduced from $\sim 800$ nm at 0.1 mW to $\sim 400$ nm at 1 mW; however, the grain boundary lines were still not observed. At powers larger than 5 mW, the grain boundary lines were observed clearly. Moreover, the defect density increased significantly and plateaued at 20 mW. The size of Ag nanoparticles reached 150–200 nm (see SI, Figure S7). Ag nanoparticles did not adsorb in the empty area even at powers higher than 20 mW.

Although point defects are visualized clearly with dark-field optics, which is a great advantage over sophisticated STM or TEM, the ability to measure the point defect density quantitatively still remains questionable. Figure 3a shows the defect density as a function of white light power. The number of Ag nanoparticles was counted for an area of 4 $\times$ 4 $\mu$m$^2$ from the optical images and averaged over several regions. The density value increased rapidly initially and plateaued to $2.47 \times 10^{11}$ cm$^{-2}$ at 20 mW. Although previous work showed the generation of defects or damages by strong laser irradiation, the power density used in this study was smaller by 10 orders of magnitude, negating the possibility of generating defects. More importantly, the plateau region at high power indicates that no new defects or damages were generated during light illumination. Such a density variance in response to the light power strongly suggests that the light promotes anchoring of Ag nanoparticles on defect sites of MoS$_2$. The number of Ag nanoparticles was counted at the plateau region to ensure the reliability of our approach. The average size of Ag nanoparticles at plateau region was 150–200 nm. To estimate the number of defects, we used the defect density obtained from the STM measurements, i.e., $4 \times 10^{11}$ cm$^{-2}$ (see SI, Figure S8). By calculating the number of defects within the Ag nanoparticles and the total area of Ag nanoparticles within a given MoS$_2$ area, the defect density obtained from our dark-field optics was $2 \times 10^{10}$ cm$^{-2}$ (see SI, calculation method). This value is lower than the measured STM value by 20 times. A similar defect-density evaluation was done with varying light exposure time at a fixed power of 60 mW, as shown in Figure 3b. The defect density reached a plateau at an exposure time longer than 10 min. The counted defect density was again very similar to the power.
dependence. This consistency in the density evaluation between light power and exposure time in the plateau region strongly indicates that the measurement of defect density is reliable and independent of the process conditions. To prove if there is any sample dependence, the CVD-grown sample was further treated by oxygen plasma (see SI, Figure S9). Defect density was modified by plasma treatment. The dark-field optical image shows the higher density of Ag nanoparticles from the oxygen plasma-treated sample. During oxygen plasma treatment, more defects are generated, and oxygen molecules are adsorbed on the defect sites. Therefore, the density of adsorbed Ag nanoparticles increased by about twice after oxygen plasma treatment. The modified defect density was clearly observed with our approaches. We conclude that our method is facile and qualitatively acceptable in estimating the change of point defect density but limitation still exists for quantitative analysis of point defects.

To evaluate the light energy dependence, several band filters were used to select wavelength of the light from white light source. The output power was ~0.13 mW in the optical range of 400−800 nm. Figure 4 shows defect visualization at various wavelengths. At 780 nm, defects were well visualized but with a lower density compared to those at higher energies. No specific grain boundary lines were formed. At 640 nm, the grain boundary lines were visible, and defect density greatly increased. The defect density reached maximum at 540 nm with clear boundary lines. For example, the light at 780 nm (1.59 eV) cannot excite electrons at the band edge because the absorption peaks for A and B peaks are located at 1.85 and 1.97 eV.2 The defects have been identified to be ~1.75 eV (measured from photoluminescence).34 We speculate that the point defects shown in Figure 4a are higher-order defects or complexes with environmental gases having the defect-related gap states below 1.59 eV. At 640 nm (1.94 eV), point defects can be directly excited and induce Ag nanoparticle adsorption. At 540 nm (2.3 eV), the increased density is strongly related to the plasmon energy of Ag nanoparticles. The plasmon energy of our sample (Ag particle size of ~200 nm) was nearly 2.4 eV, whose values slightly vary with different sizes of Ag nanoparticles (see SI, Figure S10). The plasmon-coupled incident light enhances adsorption of Ag nanoparticles on defect sites. Nevertheless, the defect density was underestimated, implying insufficient Ag supply.

The film preparation process in Figure 5a demonstrates how Ag nanoparticles are formed during the substrate preparation process. Sol−gel prepared porous TiO2 layer (thickness: 50 nm) was spin-casted on a 100 nm thick (Figure 5b) Ag film that was deposited by thermal evaporator and further annealed in air at 100 °C for 15 min. During annealing, Ag nanoparticles were embedded both within the porous TiO2 layer (middle panel in Figure 5b) and on its surface due to extended diffusion of Ag atoms (see SI, Figure S11), which was similar to previous report.35 After MoS2 was transferred in deionized water followed by drying in air and PMMA removal, large Ag nanoparticles with a size of ~300 nm below MoS2 (not visible), which are tunable with laser power as mentioned before, were formed on TiO2 surface (bottom panel in Figure 5b). EDX mapping of the cross-sectioned region near the bottom panel of Figure 5b clearly revealed the presence of Ag at the surface and below TiO2 layer (Figure 5c). Randomly distributed Ag nanoparticles were observed from the top-view FESEM image (Figure 5d). The inset shows an amplified image of the yellow region, indicating aggregates of Ag nanoparticles. The size and height profile of Ag particles measured by AFM confirms the FESEM images (Figure 5e).

It has been known that under illumination, Ag nanoparticles anchored on TiO2 substrate in aqueous solution can be dissolved in a form of Ag+ ions by transferring electrons to TiO2 layer.36 The produced Ag+ ions in solution can be further reduced and redeposited on defect sites of MoS2 to form Ag nanoparticles, in which electrons are supplied by the light illumination: Ag+ (solution) + e− → Ag0 (MoS2). This process is similar to chemically activated Ag ions on MoS2 under light illumination.36 The Ag particles with sizes of several hundred nanometers can be easily generated in our process so that they can be observed via dark-field optics. The light illumination plays a key role in promoting the related chemical reactions by an efficient charge-transfer process. The density of Ag+ ions and consequently Ag nanoparticles on MoS2 is therefore efficiently modulated by the light power/exposure time. The number of adsorbed Ag nanoparticles on the defect sites increased initially and reached a plateau due to saturated defect sites. In addition, the incident light is coupled to plasmons in Ag nanoparticles, confirmed by the strong reaction at the incident light matching with plasma frequency of Ag nanoparticles. The generation of electrons in MoS2 is another rate-determining step to Ag+ ion reduction, confirmed again the significantly reduced reaction with incident light energy smaller than the MoS2 bandgap.

To see clearly how Ag atom can be adsorbed on defect sites in MoS2, we performed density functional calculations. Two model calculations were considered for preferable Ag adsorption (Figure 6): (i) direct adsorption of Ag atom on S vacancy site and (ii) adsorption of Ag atom on oxygen atom-saturated S vacancy. Total energy calculations were performed with density functional theory (DFT) using an open source, ab initio code Quantum ESPRESSO.53 The exchange−correlation energy was described by the relativistic generalized gradient approximation (GGA) with Perdew−Burke−Ernzerhof (PBE) exchange model.54 The lattice parameter of MoS2 unit cell was 3.18 Å, and 4 × 4 supercell was fully relaxed until atomic forces were <0.05 eV/Å. A 12 × 12 × 1 Monkhost-pack grid K-point...
was used for k-point sampling. The adsorption energy was calculated by $E_{\text{ad}}(\text{Ag}) = E_{\text{total}}(\text{Ag} + \text{MoS}_2(v)) - E_{\text{total}}(\text{Ag}) - E_{\text{total}}(\text{MoS}_2(v))$. We calculate $E_{\text{ad}}(\text{Ag}) = +2.15$ eV, suggesting that simple Ag adsorption on S vacancy site is energetically unfavorable. By the similar calculations, oxygen adsorption energy on S vacancy site, $E_{\text{ad}}(\text{O}) = -8.69$ eV, forming strong chemical bonds between oxygen and Mo with a bond length of 2.07 Å. This implies that defect sites are likely saturated with oxygen atoms or molecules. Ag atom can be adsorbed on oxygen-saturated sulfur vacancy easily under ambient conditions. When Ag atom is adsorbed on oxygen-saturated sulfur vacancy, Ag adsorption energy $E_{\text{ad}}(\text{Ag--O}) = -0.51$ eV with a bond length (Ag--O) of 2.33 Å. Meanwhile, the bond length of (Mo--O) is strengthened to 2.01 Å. These calculations strongly suggest that Ag atoms can be aggregated on oxygen atom-saturated defect sites rather than directly on sulfur vacancy sites.

Figure 5. Substrate preparation process. (a) Schematic illustration of the formation and seeding of Ag nanoparticles on defect sites of monolayer MoS$_2$. (b) FESEM cross-sectional view followed by deposition processes (Ag, TiO$_2$, and MoS$_2$). (c) Cross-sectional TEM image and the corresponding EDX mapping image to identify Ag nanoparticles. (d) FESEM image of point defect distribution and enlarged point defect (inset). (e) AFM surface morphology using a tapping mode, and (f) the height profile of the Ag nanoparticle indicated by the yellow circle in (e).

Figure 6. Calculation of adsorption energy of Ag atom on defect sites. DFT-GGA calculations were performed to obtain the adsorption energy calculations. (i) Case 1: Direct adsorption of Ag atom on S vacancy and (ii) case 2: adsorption of Ag atom on oxygen atom-saturated S vacancy. The adsorption energy: $E_{\text{ad}}(\text{Ag}) = +2.15$ eV (case 1), unstable and $E_{\text{ad}}(\text{Ag--O}) = -0.51$ eV (case 2).
in MoS$_2$. The theoretical predictions are in good agreement with the increased defect density by oxidation (see SI, Figure S12).

We further demonstrate that Ag particles are adsorbed on the defect sites and grain boundaries (a collection of defects in the form of a line). Figure 7a shows a local area of empty space (left) with two MoS$_2$ grains merging in the middle of the right part. Ag nanoparticles were clearly anchored along the boundary line and edge (Figure 7c), although those Ag nanoparticles anchored at the point defects were washed out mostly during TEM grid preparation process. The grain boundary was identified by different colors at different orientations, in which two grain orientations were deviated from each other by 23° (Figure 7b).

The modification of optical properties of monolayer MoS$_2$ where Ag nanoparticles are anchored on defect sites was probed using Raman spectroscopy with 532 nm laser excitation (Figure 8). The Raman mapping image for A$_{1g}$ intensity of MoS$_2$ revealed nonuniform intensity distribution. In particular, the intensities of A$_{1g}$ near Ag nanoparticles were stronger than the other areas on bare MoS$_2$. Figure 8b shows the representative peak profiles from three different positions: MoS$_2$/SiO$_2$ substrate (bottom), MoS$_2$/TiO$_2$/Ag substrate (middle), and MoS$_2$/Ag nanoparticle/TiO$_2$/Ag. The upshift of A$_{1g}$ peak positions on Ag nanoparticles/TiO$_2$/Ag and TiO$_2$/Ag compared to that of SiO$_2$ substrate is a signature of charge compensation of n-type MoS$_2$. It is of note that E$_{1g}^2$ peak position on Ag nanoparticles/TiO$_2$/Ag was downshifted compared to those on TiO$_2$/Ag and SiO$_2$ substrate. The deconvolution of E$_{1g}^2$ peak clearly showed downshift of E$^+$ (384.6 cm$^{-1}$) with emerging E$^−$ (380.3 cm$^{-1}$) at the lower energy side. This could be explained by the tensile strain imposed by Ag nanoparticles. In addition, both Raman intensities were enhanced near Ag nanoparticles because of the high reflectance of Ag film and local electrical field enhancement by the presence of Ag nanoparticles. Figure 8c demonstrates that the intensity enhancement of A$_{1g}$ peak is

![Figure 7. TEM images of Ag nanoparticles deposited along the grain boundary of CVD-grown MoS$_2$. (a) TEM image of monolayer MoS$_2$ after decorating with Ag nanoparticle followed by transferring onto a TEM grid. Ag nanoparticles were nucleated along grain boundary and edge, (b) Selective-area electron diffraction patterns obtained on grain 1 and 2, and (c) Dark-field TEM images showing Ag nanoparticles located on the grain boundary (top) and on the edge (bottom). Many Ag nanoparticles were detached during transfer onto the TEM grid.](image)

![Figure 8. Raman characterization of CVD-grown MoS$_2$ on Ag nanoparticles using a 532 nm laser (300 μW). (a) Raman mapping image with the A$_{1g}$ peak intensity. The intensity of MoS$_2$ on Ag nanoparticles is enhanced compared to that without Ag nanoparticles and highlighted around them. (b) Raman spectra of MoS$_2$ at various positions. The substrate affects Raman peak shift and intensity. The insert graph shows downshift of E$_{1g}^2$ peak and peak split into two peaks because of the strain applied to MoS$_2$ by Ag nanoparticles. (c) Enhancement of Raman intensity and the intensity ratio (inset).](image)
larger than that of $E'_{2g}$ peak. The intensity ratio of $E'_{2g}$ peak to $A_{1g}$ peak decreased significantly to 0.2 on Ag nanoparticle/TiO$_2$/Ag substrate from ~0.8 on SiO$_2$ substrate (inset). In general, $A_{1g}$ peak intensity becomes higher by p-doping. This was done in our case by providing electrons of MoS$_2$ to Ag$^+$ ions to form Ag nanoparticles.

CONCLUSION

In summary, we successfully visualized point defects with dark-field optical microscopy by preparing a simple TiO$_2$/Ag substrate without involving heavy chemistry. Our approach provides a qualitative way of analyzing point defects and can be used to monitor defect distribution that may vary with various growth conditions of large-area TMD materials during CVD. Therefore, this method can be complementary to sophisticated STM or TEM observations and may be useful for preliminary comprehensive analysis of point defect distribution for CVD-grown TMD materials.

METHODS

Synthesis of Monolayer MoS$_2$, WS$_2$, and WSe$_2$. Ammonium heptamolybdate (AHM, Sigma-Aldrich, 431346) powder as a Mo precursor was dissolved in deionized water. The solution (6 μL) was dropped onto a quartz wafer (2 × 20 mm). The quartz wafer was put into a drying oven (~80 °C) next to the target wafer in the reactor that was coated by sodium cholate solution as described previously. S source (200 mg) was placed next to the quartz wafer and sublimated prior to growth process. The Mo heating zone was heated to 780 °C at a ramping rate of 78 °C/min, and the temperature of S zone was ramped up to 210 °C (42 °C/min). During the entire process, N$_2$ (500 sccm) was injected as a carrier gas. To synthesize tungsten dichalcogenides (WS$_2$, WSe$_2$), ammonium metatungstate hydrate (AMT, Sigma-Aldrich, 463922) as a W source was dissolved in deionized water (0.1 g/mL). Sulfur (200 mg) and selenium (500 mg) were introduced to the furnace to grow WS$_2$ and WSe$_2$, respectively. Instead of N$_2$ used in the MoS$_2$ synthesis process, hydrogen (5 sccm) was injected to reduce tungsten oxide to grow WS$_2$ and WSe$_2$. The W heating zone was heated to 800 °C at a ramping rate of 80 °C/min and maintained for 5 min. When the temperature of the W heating zone reached its maximum, S and Se zone temperature reached 210 °C and 400 °C, respectively.

Preparation of Substrate. Ag film (100 nm) was deposited by thermal evaporation on SiO$_2$/Si substrate. The titanium(iv) butoxide (TiO$_2$, Sigma-Aldrich, 510718, 5 wt % in n-butanol) was spin-coated (2000 rpm, 60 s) onto the Ag/SiO$_2$/Si substrate and annealed at 100 °C for 15 min in air. During annealing, Ag nanoparticles were formed on the surface of TiO$_2$ layer by diffusion through porous TiO$_2$ layer.

Decoration of Ag Nanoparticles on Defective Sites of TMDs. The CVD-grown TMDs were transferred to TiO$_2$/Ag/SiO$_2$/Si substrate with PMMA support. The PMMA A4 (MicroChem, 4 wt % in anisole) was spin-coated onto the as-grown TMDs/SiO$_2$ (at 1500 rpm for 60 s). The TMDs and PMMA support were detached from SiO$_2$ by placing the TMDs/SiO$_2$ into a hot 1 M KOH solution for a few minutes. PMMA/TMD layer was then detached from SiO$_2$/Si substrate and then floated onto the KOH solution. Next, the PMMA/TMDs were rinsed using deionized water for 4 times. Finally, the PMMA/TMDs were picked up by the prepared substrate and then illuminated using a white light source (LDLS EQ-99FC) for 20 min. The light intensity and wavelength were controlled using a neutral density (ND) filter (0.1–200 mW) and a band filter (420–780 nm). During illumination, Ag ions were diffused to the defect sites of TMDs. PMMA was removed by acetone, and the sample was rinsed with isopropyl alcohol (IPA) and deionized water for several times.

TEM Sample Preparation. The sample was transferred to a quartz TEM grid with a copper-supported thin film (TedPella, 200 mesh, copper, 1.2 mm holes). After Ag nanoparticle decoration under PMMA/MoS$_2$ film during white light irradiation, the PMMA/MoS$_2$ film with substrate was immersed into deionized water, fixed using a TEM grid, and dried under ambient conditions. PMMA was then removed by acetone, and the sample was rinsed with IPA.

Characterization. The morphology of TMDs on TiO$_2$/Ag was examined using optical microscopy (20X and 100X magnification, WEISS, Axios Imager 2), AFM (Nano Navi) in tapping mode, and FESEM (JEOL JSM7000F). Raman mapping was performed using confocal Raman microscopy (NTEGRA Spectra, NT-MDT) system with an exciting laser wavelength of 532 nm and a 100X objective (NA = 0.7) lens. The microstructure of MoS$_2$ was obtained using TEM (JEOL ARM 200 F). Focused ion beam (SII SMI3050TB) was used to visualize elements of nanoparticle and their cross-sectional structures.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b05854.

Supporting figures S1–S12 and calculation method (PDF)

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Notes

The authors declare no competing financial interest.

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