

Research Article

Improvement of Mechanical Characteristics on Ultra-High Molecular Weight Polyethylene Surface through Zinc Oxide Atomic Layer Deposition Film

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Received 27 June 2022; Revised 13 October 2022; Accepted 15 November 2022; Published 13 December 2022

Academic Editor: José António Fonseca de Oliveira Correia

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Wear failures in ultra-high molecular weight polyethylene (UHMWPE) compartments are known to limit the life of a joint implant. In this study, we applied atomic layer deposition (ALD) technique to produce wear-resistant zinc oxide (ZnO) films to improve mechanical and wear characteristics on the surface of UHMWPE. Organic material layers in molecular units were mixed with ALD ZnO films to minimize surface cracks through a molecular layer deposition (MLD) technique. We aimed to examine (1) the effect of organic layers on minimizing surface cracks and (2) the mechanical properties of ZnO and inorganic/organic hybrid films. We prepared UHMWPE samples with pure ZnO and five different hybrid films with ZnO to organic layer ratios of 1:1, 2:1, 3:1, 4:1, and 5:1. Surface cracks were observed by using a field-emission scanning electron microscope. Hardness and elastic modulus of an ALD-coated UHMWPE were measured by nano-indentation examinations. Severe cracks were found in the samples with pure ZnO films. However, no cracks were found in the samples with all hybrid films except the samples with a ZnO to organic layer ratio of 5:1. The hardness and elastic modulus of the samples with pure ZnO and hybrid films significantly increased compared to those of the native UHMWPE. The hardness to elastic modulus ratios, indicating the wear resistance, increased over 50% for all films compared to the values of native UHMWPE. These results suggested that ALD ceramic coatings with organic layers may become a potential solution for realizing a wear-resistant protection coating for the polymer compartment of joint prostheses.

1. Introduction

Polymer materials have been widely used in biomedical applications owing to their light weight, structural rigidity, conformability, electromagnetic inactivity, biochemical stability, and biocompatibility [1, 2]. However, the polymer material applications are limited by minimal loading conditions because the mechanical strength of polymers is generally inferior to that of common metal-based materials [3–5]. A joint prosthesis is an application that requires mechanical properties to resist body weight and abrasive wears on articulating surfaces. Although ceramic materials are ideal for minimizing wear damage, the brittle and nonconformable characteristics of ceramics often lead to fractures in joint implants [6, 7]. Thus, modern joint prostheses are designed to form an articulating surface

between metal (cobalt-chromium alloy) and ultra-high molecular weight polyethylene (UHMWPE) compartments. The high crack resistance and toughness of UHMWPE [8–10] are useful in preventing highly concentrated contact stresses on articulated surfaces. However, wear failures in relatively weak UHMWPE compartments are known to limit the life of a joint implant [11]. Gamma irradiation and vitamin E stabilization techniques are widely used to improve the wear characteristics of UHMWPE by increasing the cross-linking between molecular chains [12–14]. However, the life of joint prostheses is not sufficient for clinical implementation.

Atomic layer deposition (ALD) is a popular method to create mechanically strong ceramic films on the surface of various materials at relatively low temperatures [15, 16]. Because conventional surface coating methods such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) require high-temperature conditions that are generally much higher than the melting temperature of polymers [17–19], the ALD process can be considered as a potential solution to form wear-resistant ceramic layers on the surface of UHMWPE structures without causing thermal damage to native polymer chains [20-22]. Previous studies have reported the mechanical effects of ALD ceramic films on the surface of various materials. Aluminum, titanium, and zinc oxide (ZnO) layers have been shown to significantly increase the hardness and elastic modulus of wafer and glass surfaces [23-26]. Aluminum oxide films on polyethylene naphthalate have been examined for the improvement of critical strain energy in crack propagation [27]. ZnO films have been reported to decrease the friction coefficient and increase the wear resistance of stainless steels [28].

Adhesion failures between ALD films and underlying materials are a common problem when there are large differences in the thermal expansion coefficients of each material [29]. Different thermal contraction ratios in the two materials may create separations between the ALD films and the underlying materials, which may result in multiple cracks on the surface of the ALD films [30, 31]. Recent studies introduced mixtures of ALD films and organic material layers in molecular units through a molecular layer deposition (MLD) process to minimize adhesion problems owing to mismatches in the thermal expansion coefficients [31]. Composing organic MLD layers using trimethylaluminum with ethylene glycol has shown significant reductions in the surface damage of aluminum oxide ALD films on Teflon-fluorinated ethylene propylene [31]. Because differences in the thermal expansion coefficients of ceramics (ZnO: $1.57 \times 10^{-5} \text{ K}^{-1}$, aluminum oxide: $1.03 \times 10^{-5} \text{ K}^{-1}$) and UHMWPE $(18 \times 10^{-5} \text{ K}^{-1})$ are distinct, MLD organic layers might be a good solution to reduce surface failures on ALD ceramic films.

Although previous ALD studies have primarily focused on microelectronics applications, our goal is to improve the mechanical properties of polymer surfaces by creating ceramic films on the surface of polymer structures. In this study, we aimed to examine the improvements in the mechanical properties of UHMWPE surfaces after applying ZnO and organic material hybrid film. We decided to use ZnO as the material for ceramic films because ZnO is known to effectively reduce the coefficient of friction of articular surfaces [32-34]. ZnO nanoparticles have been widely used for the delivery of biomolecules [35-37], treatments of various diseases [38, 39], and tissue engineering applications [40, 41]. Biocompatibility and toxicity of ZnO-related materials are already well proven [42, 43]. We tested (1) the effect of MLD organic layers on minimizing surface failures and (2) the mechanical properties of ZnO hybrid films with different ratios of ZnO and organic buffer layers. Finally, we aimed to estimate whether ALD ceramic films could be a potential solution for improving the wear characteristics of polymer compartments in joint prostheses.

2. Methods

2.1. Sample Preparation. We prepared $15 \times 15 \times 5 \text{ mm}^3$ UHMWPE (Mitsubishi Chemical group, Tokyo, Japan) blocks (Figure 1(a)). The surface roughness of all the samples was controlled by a five-step sanding process with sandpapers of #200, #400, #800, #1600, and #2400 grits in a sequential order. Final polishing was performed using a polishing cloth with a 1 μ m diamond suspension solution. The polished specimens were cleaned with isopropyl alcohol and distilled water for 10 min in an ultrasonic washing machine (JAC Ultrasonic KODO, Yong In, Korea). We then applied O₂ plasma treatment (Femto Science, Hwaseong, Korea) to the surface of the UHMWPE blocks for 60 s with a discharging power of 100 W to improve chemical reactions of UHMWPE with coating materials.

2.2. ALD Window for ZnO Layers on UHMWPE. The deposition rate of the ZnO layer on the UHMWPE blocks was measured at different working temperatures between 60°C and 120°C, below the melting temperature of UHMWPE (130°C). A total of 450 cycles of ZnO deposition were applied to all the samples, and the thickness of the ZnO layers was measured.

2.3. ALD and MLD Processes. A custom holder for UHMWPE specimens was developed for the effective and uniform heating of the polymer samples. Two metal bars were placed in contact with both sides of the polymer block to transmit heat energy through the side and bottom surfaces of the sample (Figure 1(b)). All samples were preheated for an hour at 100°C, as determined from the ALD window examination results. First, we created UHMWPE samples with pure ZnO films. The precursor for the ZnO layer was diethylzinc (DEZ, EG Chem, Gongju, Korea). The ZnO ALD process consisted of alternating pulses of DEZ and distilled water (H₂O). Nitrogen gas (N₂, 99.99%) was used to purge the gases remaining inside the chamber between the DEZ and H₂O pulses. Thus, a complete ZnO deposition cycle consisted of sequential pulsing of DEZ, N2, H2O, and N2 for 0.5, 30, 0.5, and 30 seconds, respectively. The ZnO ALD deposition cycle was repeated 1200 times. The chemical reactions in the ZnO layers are expressed in the following formulas (the asterisks denote the surface groups).

$$Zn(CH_2CH_3)_2 * + H_2O \longrightarrow OZn(C_2H_5) * + C_2H_6\uparrow$$
$$OZn(C_2H_5) * + H_2O \longrightarrow OZn(OH) * + C_2H_6\uparrow.$$
(1)

We also fabricated UHMWPE samples with hybrid films of ZnO and organic layers. The deposition process of the organic layer was similar to that of pure ZnO films, but H_2O was replaced with hydroquinone (HQ, Sigma-Aldrich Chemistry, St. Louis, USA). A complete organic layer deposition cycle consisted of sequential pulsing of DEZ, N₂, HQ, and N₂ for 0.5, 30, 0.5, and 60 seconds, respectively. The chemical reactions in the organic layers are expressed in the following formula.



FIGURE 1: (a) A UHMWPE sample and (b) the custom holder are shown.

$$OZn(C_2H_5) * + HO - R - OH \longrightarrow OZn(O - R - OH) * + C_2H_6^{\uparrow}.$$
(2)

We controlled the ratio of the ZnO and organic layers by changing the number of cycles in each layer (Figure 2). A single layer of ZnO or organic material was designed to be formed with a thickness of 0.3 nm. Five sample groups with different ZnO to organic layer ratios were prepared (ZnO to organic layer ratios of 1:1, 2:1, 3:1, 4:1, and 5:1), and the entire deposition cycle was maintained for 1200 cycles for all specimens. At the end of the deposition process, the deposition chamber was gradually cooled to room temperature for 180 min to minimize the thermal stresses in the samples.

2.4. Coating Characterization. Surface images of the ALDcoated UHMWPE samples were acquired using a fieldemission scanning electron microscope (FE-SEM; FEI Quanta 250 FEG, Philips, Amsterdam, Netherlands). The thicknesses of the ALD film layers were measured using focused ion beam scanning electron microscopy (FIB-SEM; LYRA3 XMH, TESCAN, Brno, Czech Republic). The chemical characteristics of the ALD film layers were analyzed using grazing incidence X-ray diffraction (GIXRD; Smart Lab, Rigaku, Tokyo, Japan) with an X-ray power of 9 kW and a wavelength of 0.15 nm. Fourier transform infrared spectroscopy (FTIR; Cary 630, Agilent, Santa Clara, CA, USA) was used to measure the spectrum of the molecular structures in the ALD films (frequency range: $650-4000 \text{ cm}^{-1}$, frequency interval: 2 cm^{-1}). The hardness and elastic modulus of an ALD-coated UHMWPE surface were measured by nano-indentation examinations (UNHT³, Anton Parr, Graz, Austria) at 15 randomly selected locations in a sample. The indentation depth was determined to be 25% of the entire ALD film thickness for each specimen.

2.5. Scratch Test of ZnO Films. Scratch tests of ZnO films were performed by using a nano-scratch device (UNHT3, Anton Parr, Graz, Austria) to examine adhesion characteristics of pure ZnO and hybrid ZnO (ZnO:organic layer = 1:1) films on the surface of UHMWPE. A normal compressive load was gradually increased from 0 to 600 mN through a scratch length of 3 mm with a scratch speed of 6 mm/min. A Rockwell diamond tip with a tip radius of 50 μ m was used to provide a maximum contact pressure of approximately 64 MPa (Hertzian contact theory) which was comparable to



FIGURE 2: Ratios of the ZnO and organic layers were controlled by changing the number of cycles in each layer. An example of ZnO: organic layer = 3:1 is presented.

the contact pressure of 20–30 MPa in total knee arthroplasty [44]. Energy dispersive spectrometer (EDX) technique was used to measure atomic ratios of ZnO films in and outside of the scratch tracks. Locations of EDX measurements were indicated by star (*) symbols in Figure 3.

3. Results

3.1. ALD Window. The growth rate of the ZnO layers on the UHMWPE surface was observed at different temperatures (Figure 4). The growth rate gradually increased and stabilized at a chamber temperature of 100° C. Thus, we decided to use 100° C as the ALD processing temperature for subsequent experiments.

3.2. Chemical Analysis. GIXRD measurements of the samples with pure ZnO films showed three distinct peaks at 31.8°, 34.5°, and 36.3°, which are indicators of the wurtzite crystal structures representing the degree of crystallinity of the ZnO layers [45–47]. These three peaks gradually decreased as the ratio of ZnO to the organic layer decreased (Figure 5(a)). A (020) peak around 30°, which is one of typical diffraction signals of UHMWPE, is also shown [48, 49].

FTIR measurements of the samples with hybrid films showed strong absorbance peaks at 788 cm^{-1} , 827 cm^{-1} , 1204 cm^{-1} , and 1492 cm^{-1} wavenumbers, indicating Zn-O,



FIGURE 3: SEM images and load-deformation curves of scratch tests for (a) pure and (b) hybrid ZnO films are shown. Locations of EDX measurements for atomic ratios in and outside of the scratch tracks were indicated by star (*) symbols.



FIGURE 4: Growth rate of the ZnO layers on the UHMWPE surface was shown at different temperatures.

C-H, C-O, and C = C aromatic stretching modes in organic materials, respectively [50–52]. These peaks increased as the ratio of ZnO to the organic layer decreased (Figure 5(b)). Additional distinct peaks around 750 cm^{-1} and 1450 cm^{-1} indicate CH₂ rocking of methyl and CH bending of methylene groups in UHMWPE [53–55].

3.3. Surface Images of UHMWPE with Various ZnO Films. The FE-SEM images of the UHMWPE samples with different ALD films are shown in Figure 6. Roughness of UHMWPE surfaces seemed to change with hybrid films of ZnO and organic layers. It might be that ZnO grains and organic HQ-DEZ bonding structures increased irregularity of surface profiles. However, the size and distribution of the ZnO grains were uniform throughout all the samples. However, severe cracks on the surface of the ZnO films were distinct in the samples with pure ZnO films (Figure 6(g), ZnO 100%). Although surface cracks were found in the samples with a ZnO to organic layer ratio of 5:1 (Figure 6(f), ZnO:organic layer = 5:1), no cracks were found in hybrid film samples with other ratios.

3.4. Mechanical Properties. The thickness of the ALD films was approximately 200 nm (Table 1). The hardness and elastic modulus of the UHMWPE samples with pure ZnO films significantly increased compared to those of the native UHMWPE blocks (Tukey's HSD post hoc significant difference test, p < 0.01, Figures 7(a) and 7(b)). The hardness and elastic modulus of the UHMWPE specimens with hybrid films were significantly greater than those of the native UHMWPE (Tukey's HSD test, p < 0.01), but significantly smaller than the values in the samples with pure ZnO films (Tukey's HSD test, p < 0.01). Differences in hardness and elastic modulus observe the samples with pure ZnO films (Tukey's HSD test, p < 0.01). Differences in hardness and elastic modulus values between hybrid films with different ZnO to organic layer ratios were not significant (Tukey's HSD test, p > 0.05).



FIGURE 5: (a) GIXRD, and (b) FTIR measurements of pure ZnO film and hybrid films with various ratios are shown.

The hardness to elastic modulus ratios (H/E ratio), indicating the wear resistance of a solid material [56, 57], were calculated for different films (Figure 7(c)). The H/E ratios increased for all types of ALD films compared to the values of native UHMWPE (Tukey's HSD test, p < 0.01). Although pure ZnO films showed higher H/E ratios than the hybrid films, the differences were not significant except for 4:1 hybrid film sample (Tukey's HSD test, p > 0.05).

3.5. Scratch Characteristics. SEM images of the scratches on UHMWPE surfaces with pure ZnO and hybrid ZnO films are shown in Figure 3. Changes in indentation loads and displacements during scratch tests are also shown for both pure and hybrid ZnO films (Figure 3). Multiple cracks were prominent from the early stage of the scratch, and the crack patterns became severer as the compressive load increased on the pure ZnO film (Figure 3(a)). However, no surface cracks were found throughout the entire scratch track on the hybrid ZnO film (Figure 3(b)). We were unable to measure distinct critical loads for failures in both types of films. EDX measurements revealed that atomic ratio of Zn was reduced by approximately 20% in the scratch track for pure ZnO films. However, the difference in atomic ratios of Zn in and outside of the scratch track was minimal for hybrid ZnO films (Table 2).

4. Discussion

We successfully produced ceramic films with ZnO on the surface of UHMWPE using ALD, which is suitable for polymers because of its relatively low processing temperature. ZnO ceramic layers were shown to improve the mechanical and wear characteristics of the polymer surfaces. Organic layers were applied between each ZnO layer to minimize surface failures of ceramic films, which might be caused by mismatches in thermal expansion ratios of different materials. The sandwich-type hybrid ceramic films of ZnO and organic layers (Figure 2) significantly increased the hardness and elastic modulus of the native UHMWPE samples. Although the mechanical properties of the hybrid films were inferior to those of the pure ZnO films, the hybrid films resulted in markedly reduced crack failures on the surface of the ceramic films. Moreover, the H/E ratio as an indicator of wear resistance in a solid material [58, 59] was significantly improved in the samples with hybrid films of ZnO and organic layers. The H/E ratios of the hybrid films were comparable to those of pure ZnO films (Figure 7(c)).

The formation of ZnO film layers on UHMWPE surfaces was tested using GIXRD to measure the degree of crystallinity of ZnO. Distinct wurtzite crystal peaks at 31.8°, 34.4°, and 36.3° in the GIXRD measurements of the pure ZnO films indicate the formation of ZnO layers [60, 61]. These peaks were undetectable (31.8° and 34.4°) or decreased (36.3°) in the films with organic layers. Because only a few cycles of ZnO (one to five ZnO cycles in the films with different ZnO to organic layer ratios) existed between each organic layer in the hybrid films, the diffraction signals of the ZnO crystal peaks may be weaker than those for the pure ZnO thick films (Figure 5(a)). The formation of organic layers was also examined by FTIR by measuring the characteristic frequencies (788 cm⁻¹, 827 cm⁻¹, 1204 cm⁻¹, and 1492 cm⁻¹) of HQ rings in the hybrid films [50, 62]. Strong peaks at these frequencies in all the hybrid films suggest the stable formation of phenylene HQ rings [50, 62]. Increases in the signals for HQ frequencies for the films with greater buffer layer proportions also indicated the successful control of the buffer layers in our ALD design.

ZnO and organic layer hybrid films exhibited significant reductions in surface cracks, although severe surface cracks were found in all tested samples with pure ZnO layers. Surface failures on pure ZnO films might be the result of



FIGURE 6: FE-SEM images of the UHMWPE samples with different ALD films are shown. (a) Native UHMWPE. (b) ZnO: organic layer = 1: 1. (c) ZnO: organic layer = 2:1. (d) ZnO: organic layer = 3:1. (e) ZnO: organic layer = 4:1. (f) ZnO: organic layer = 5:1. (g) ZnO 100%.



TABLE 1: Thickness of pure and hybrid ZnO films.

FIGURE 7: (a) Hardness, (b) elastic modulus, and (c) H/E ratio of pure ZnO and hybrid films are shown.

	Location	Atomic weight (%)	
		Zn	С
Pure ZnO film	Outside the scratch	51.85	30.73
	Inside the scratch	40.87	43.64
Hybrid ZnO film	Outside the scratch	9.85	77.12
	Inside the scratch	9.54	81.51

TABLE 2: Atomic weight ratios in and outside of scratch tracks for pure and hybrid ZnO films.

differences in the thermal expansion coefficient between ZnO $(1.57 \times 10^{-5} \text{ K}^{-1})$ and UHMWPE $(18 \times 10^{-5} \text{ K}^{-1})$ [63]. Because the thermal expansion coefficient of UHMWPE is approximately 11 times greater than that of ZnO, thermal contractions in the UHMWPE surface must be greater than those in ZnO films during the cooling stage of the ALD

process. Mismatches in the thermal contraction between the two materials may create compressive stress on the ZnO films and result in surface cracks [30, 31]. Continuous uplift patterns surrounding the surface cracks provided strong evidence for the formation of compressive stresses in the pure ZnO films (Figure 6(g)). A mixture of organic layers in every few cycles of ZnO films may act as cushions to release compressive stresses and reduce surface failures. However, these cushion effects of the organic layers seemed to decrease as the proportion of ZnO layers increased because surface cracks started to appear in the samples with a ZnO to organic layer ratio of 5:1 (Figure 6(f)). Further studies are needed to determine the optimum ratio between ZnO and the organic layers for protection against surface failure.

The mechanical properties of both the pure and hybrid ZnO films were significantly better than those of the native UHMWPE samples. ZnO ceramic films on the surface of UHMWPE could protect UHMWPE structures from mechanical contact damage. Although the organic layers reduced the surface cracks, the mechanical properties (hardness and elastic modulus) of the hybrid films decreased by approximately 30% to 40% from the properties of pure ZnO films (Figures 7(a) and 7(b)). Reductions in the mechanical properties of the hybrid films might be inevitable because the proportion of ZnO layers is reduced [64]. Although the hardness and elastic modulus of the hybrid films decreased, the H/E ratios remained similar in both the pure and hybrid ZnO films (Figure 7(c)). Because the wear characteristics on a solid surface are known to be described by H/E ratios, these results indicate similar wear resistances in both films.

ZnO and organic material hybrid films exhibited markedly improved scratch characteristics. EDX measurements in the scratch tracks showed reductions in atomic ratio of Zn for pure ZnO films, suggesting delamination of ZnO film under a physiologic level of contact pressure (64 MPa) while the differences in Zn atomic ratios in and outside of the scratch were minimal for hybrid ZnO films. Numerous cracks inside the scratch on pure ZnO films might be the result of brittle failures from a large magnitude of vertical compression and deformation. However, organic MLD layers in the hybrid ZnO films may increase the ductility of thin films and resulted in reduced crack failures inside the scratch [65, 66]. In this study, we were unable to measure distinct critical loads for film failures. It might be the result of thick specimens (approximately 7 mm thick) of soft UHMWPE material to simulate the contact situation in a real joint prosthesis. Because vertical deformation in a thick material would be larger than the deformation in a thin film, our ZnO films may also deform through the profile of vertical deformation in UHMWPE blocks prior to a complete delamination of the films [67, 68]. Our scratch test configuration was different from previous studies on thin film-type substrates which resulted in small vertical deformations and distinct critical loads for failures [69]. However, our examination on thick UHMWPE blocks might be a better representation of realistic contact mechanics in physiologic environments for joint prostheses.

This study has some limitations that need to be addressed. First, we applied only one cycle of the organic layer between ZnO films, although the deposition cycle of ZnO varied from one to five cycles in different types of hybrid films. Our results suggest that organic layers reduce the thermal stresses on ZnO layers and minimize surface cracks. Thus, multiple cycles of organic layers may result in better resistance to surface cracks in ceramic films. However, we did not examine multiple cycles of organic layers because the goal of this study was to establish the relationship between the proportion of organic layers and the reduction in surface cracks within a ceramic film. Further studies on hybrid films with multicycle organic layers are important to understand the optimal deposition conditions for various ceramic films. Second, the wear resistance of the ZnO ceramic films was estimated from the H/E ratios from the nano-indentation examination results. The wear characteristics of a solid material are generally

examined by measuring the volume or weight loss in the sample after ball-on-disk- or pin-on-disk-type wear tests [70–72]. Unfortunately, measurement of volume or weight losses in nanoscale films was not possible. Thus, we described the changes in wear characteristics of ALD films using H/E ratios, which have been widely used as an indicator of wear resistance [29]. Although future ball-on-disk or pin-on-disk wear studies on thicker films would reveal the improvement in wear characteristics by measuring volume or weight losses in the films, we believe that the current results of H/E ratios may still be useful for estimating changes in wear characteristics after ALD ceramic film coating on polymer materials.

5. Conclusion

In this study, we created ALD ZnO films on the surface of UHMWPE to improve the mechanical and wear characteristics of UHMWPE samples, and organic layers were mixed with ZnO films to reduce surface damage. The organic layers exhibited excellent reductions in the surface cracks in the ALD ZnO films and significantly increased the hardness and elastic modulus of the UHMWPE surfaces. The wear resistance of the hybrid films with ZnO and organic layers was also significantly increased and was comparable to the value measured for pure ZnO films. Because biomedical applications of polymers have been limited in nonweightbearing situations due to their poor wear characteristics, our ALD ceramic coating approach should be a method to improve the mechanical characteristics on the surface of polymer materials without causing chemical and thermal damage to native polymer structures. Although further research on macroscale mechanical examinations needs to be conducted, several promising results from this study suggest that the ALD ceramic layer with organic layer on polymer surfaces may become a potential solution for realizing a wear-resistant protection coating for the polymer compartment of joint prostheses.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea Government (MSIT) (2019R1A2C1011673).

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