Combustion Synthesis of NbB$_2$–Spinel MgAl$_2$O$_4$ Composites from MgO-Added Thermite-Based Reactants with Excess Boron

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Received: 24 February 2020; Accepted: 17 March 2020; Published: 18 March 2020

Abstract: The formation of NbB$_2$–MgAl$_2$O$_4$ composites from the MgO-added thermite-based reaction systems was investigated by self-propagating high-temperature synthesis (SHS). Two thermite mixtures, Nb$_2$O$_5$/B$_2$O$_3$/Al and Nb$_2$O$_5$/Al, were, respectively, adopted in Reactions (1) and (2). The XRD analysis confirmed the combination of Al$_2$O$_3$ with MgO to form MgAl$_2$O$_4$ during the SHS process and that excess boron of 30 atom.% was required to yield NbB$_2$–MgAl$_2$O$_4$ composites with negligible NbB and Nb$_3$B$_4$. The microstructure of the composite reveals that rod-shaped MgAl$_2$O$_4$ crystals are closely interlocked and granular NbB$_2$ are embedded in or scattered over MgAl$_2$O$_4$. With the addition of MgAl$_2$O$_4$, the fracture toughness ($K_{IC}$) of 4.37–4.82 MPa m$^{1/2}$ was obtained for the composites. The activation energies $E_a = 219.5 \pm 16$ and 167.9 ± 13 kJ/mol for Reactions (1) and (2) were determined from combustion wave kinetics.

Keywords: boride NbB$_2$; spinel MgAl$_2$O$_4$; combustion synthesis; microstructure; thermite

1. Introduction

Transition metal (IVB and VB) diborides, such as TiB$_2$, ZrB$_2$, NbB$_2$, and TaB$_2$, have been referred to as ultra-high-temperature ceramics (UHTCs). Transition metal diborides crystallize in the hexagonal A1B$_2$ type structure (space group P6/mmm) with c/a ratio close to unity. In this arrangement, the hexagonal nets of metal atoms and triangle nets of pure boron atoms are alternately stacked along the c axis [1]. Besides their melting points exceeding 3000 °C, they possess a unique combination of high hardness, thermal conductivity, electrical conductivity, excellent chemical stability, corrosion resistance, and thermal shock resistance [2–5]. They have found a broad range of applications in the mechanical, automobile, aerospace industries, etc. [5]. To improve the refractory properties of metal borides and carbides, Al$_2$O$_3$ or MgAl$_2$O$_4$ (magnesium aluminate spinel) has been considered as an additive. Extensive studies have been conducted on understanding the production and characteristics of different metal borides reinforced by Al$_2$O$_3$ [6–10], but relatively few studies have focused on the boride–MgAl$_2$O$_4$ composite [11].

MgAl$_2$O$_4$ is of particular interest due to its exceptional mechanical, thermal, and optical properties, such as high melting point (2135 °C), high hardness (16 GPa), relatively low density (3.58 g/cm$^3$), high mechanical strength (135–216 MPa), good transmittance in the wavelength range of 0.25 to 5.0 μm, high thermal shock resistance, high chemical inertness, low dielectric constant, and low thermal expansion coefficient [12,13]. MgAl$_2$O$_4$ spinel has a close-packed face-centered cubic (fcc) structure of space group $Fd3m$ (number 227). There are eight MgAl$_2$O$_4$ units per cubic cell. Mg and Al cations occupy 1/8 of the tetrahedral sites and 1/2 of the octahedral sites and there are 32 oxygen ions in the unit cell. In the normal spinel, all Al$^{3+}$ ions are in octahedral coordination with local symmetry D$_{3d}$.
and all Mg$^{2+}$ ions are in tetrahedral coordination with point group symmetry $T_d$. The anion sublattice is arranged in a pseudo-cubic close-packed (ccp) spatial configuration. There are four layers of $\text{AlO}_6$ octahedral chains along the $c$ axis in one unit cell [12]. Fabrication of MgAl$_2$O$_4$ and other spinel compounds like NiFe$_2$O$_4$ and CoFe$_2$O$_4$ by either solid-state or wet-chemistry reaction methods usually requires long processing time and complicated steps [14–18].

With the merits of energy and time savings, simple operation, and high-purity products, combustion synthesis in the mode of self-propagating high-temperature synthesis (SHS) has been recognized as an alternative route to material synthesis and processing [19,20]. When the SHS process is combined with the aluminothermic or magnesiothermic reduction of metal oxides to generate Al$_2$O$_3$ or MgO, the multistage combustion reaction represents an in situ approach to producing MgAl$_2$O$_4$-containing composites [21–25]. Horvitz and Gotman [21] obtained TiAl–Ti$_3$Al–MgAl$_2$O$_4$ composites from the powder compacts composed of $2\text{TiO}_2$–Mg–$4\text{Al}$ via the SHS reaction and thermal explosion. Magnesiothermic reduction of WO$_3$ and B$_2$O$_3$ in the presence of Al$_2$O$_3$ under the SHS manner was conducted by Omran et al. [22] to prepare MgAl$_2$O$_4$–W and MgAl$_2$O$_4$–W–$2\text{B}$ composites. With the use of MoO$_3$, Si$_2$O$_2$, and Al as the thermite reagents mixing with Mo, Si, and MgO powders for the SHS reaction, the formation of various molybdenum silicides (MoSi$_2$, Mo$_5$Si$_3$, and Mo$_2$Si) and MgAl$_2$O$_4$ composites was achieved [23–25].

This study made an attempt to investigate the preparation of Nb$_2$B$_2$–MgAl$_2$O$_4$ in situ composites via a reduction-based SHS process. The multistage combustion process involves the aluminothermic reduction of Nb$_2$O$_5$ and B$_2$O$_3$ in the presence of MgO, elemental interaction of Nb with B, and the combination of MgO with Al$_2$O$_3$. To resolve the loss of boron in the form of gas-phase B$_2$O$_3$ and BO during the SHS process [8,9], this study examined test specimens with excess boron. The effects of thermite reagents and excess boron on the reaction exothermicity and combustion wave kinetics were explored. Moreover, the phase composition, microstructure, and mechanical properties of the final products were characterized.

2. Materials and Methods

The starting materials utilized by this study included niobium (V) oxide (Nb$_2$O$_5$) (Strem Chemicals, <45 µm, 99.9%, Newburyport, MA, US), B$_2$O$_3$ (Strem Chemicals, 99.9%), Al (Showa Chemical Co., <45 µm, 99.9%, Tokyo, Japan), Nb (Strem Chemicals, <45 µm, 99.8%), amorphous boron (Noah Technologies Corp., <1 µm, 92%, San Antonio, TX, US), and MgO (Alfa Aesar, 99%, Ward Hill, MA, US). Two MgO-added combustion systems with different thermite reagents were studied. As expressed below, Reaction (1) comprises Nb$_2$O$_5$ and B$_2$O$_3$ as thermite oxidants, while Reaction (2) has Nb$_2$O$_5$ only. For both reaction systems, Al acts as the thermite reductant.

\[ \frac{x}{2} \text{Nb}_2\text{O}_5 + \left(1 - \frac{5}{6}x\right)\text{B}_2\text{O}_3 + 2\text{Al} \rightarrow \left(\frac{11}{3}x - 2\right)\text{B} + \text{MgO} \rightarrow x\text{NbB}_2 + \text{MgAl}_2\text{O}_4 \quad (R1) \]

\[ \left(\frac{3}{5}\text{Nb}_2\text{O}_5 + 2\text{Al}\right) + \left(y - \frac{6}{5}\right)\text{Nb} + 2y\text{B} + \text{MgO} \rightarrow y\text{NbB}_2 + \text{MgAl}_2\text{O}_4 \quad (R2) \]

where $x$ and $y$ are stoichiometric coefficients signifying the mole number of NbB$_2$ formed per unit mole of MgAl$_2$O$_4$ in Reactions (1) and (2), respectively.

The experiments of Reaction (1) were performed with $x = 0.6$–1.0. The increase of $x$ raises the amount of Nb$_2$O$_5$ but reduces that of B$_2$O$_3$ in the reactant mixture. Under this condition, more amorphous boron is added to make up for the decrease of boron provided from B$_2$O$_3$. Samples of Reaction (2) were formulated with $y = 1.2$–1.8. The increase of $y$ augments elemental Nb and B for the production of a larger amount of NbB$_2$, but has no change in the molar quantity of thermite reagents, Nb$_2$O$_5$ and Al, in Reaction (2). A combination of Reactions (1) and (2) renders this study feasible to obtain products with a molar proportion of NbB$_2$/MgAl$_2$O$_4$ from 0.6 to 1.8. In addition, the SHS reactions with test specimens containing excess boron of 20 and 30 atom.% were conducted to examine the extent of boron loss during combustion and to compensate for the relatively low purity (92%) of
amorphous boron used in this study. It should be noted that boron has high hardness, great stability in extreme environments, and good resistance to heat. It has several forms, the most common of which is amorphous boron, and is unreactive to oxygen, water, acids, and alkalis. While barely reactive at room temperature, boron reacts strongly at high temperature with metals to form borides. Moreover, its reducing properties allow it to react with numerous compounds and, as in the case of oxygenated or halogenated compounds, in a violent manner [26].

In Reaction (1), the aluminothermic reduction of Nb₂O₅ (the reaction enthalpy, ∆Hᵣ = −536 kJ/mol of Al₂O₃ and the adiabatic temperature, T_ad = 2756 K) is more energetic than that of B₂O₃ (∆Hᵣ = −403.8 kJ/mol of Al₂O₃ and T_ad = 2315 K) [27,28]. The intermetallic reaction of Nb + 2B to yield NbB₂ with formation enthalpy ∆Hᵣ = −175.3 kJ/mol and T_ad = 2315 K is exothermically comparable to the B₂O₃ + 2Al reaction [29]. The combination reaction between MgO and Al₂O₃ to form MgAl₂O₄ is weakly exothermic with ∆Hᵣ = −35.6 kJ [23]. This means that with the increase of NbB₂ content (the x value), two opposing effects govern the combustion exothermicity of Reaction (1). As far as Reaction (2) is concerned, the increase of y for the formation of a larger NbB₂ content has a dilution effect on combustion. To elucidate the combustion exothermicity, calculation of T_ad of Reactions (1) and (2) under different stoichiometric coefficients was performed according to the following equation [23,30] with thermochemical data taken from [29].

$$\Delta H_r + \int_{298}^{T_{ad}} \sum n_i C_p(P_j) dT + \sum_{298-T_{ad}} n_j L(P_j) = 0$$

where ∆Hᵣ is the reaction enthalpy at 298 K, nᵢ is the stoichiometric constant, C_p and L are the heat capacity and latent heat, and P_j refers to the product. Calculations of the adiabatic temperature were based upon the final products of stoichiometric reactions described in R(1) and R(2).

Reactant powders were mixed in a ball mill and then uniaxially compressed in a stainless-steel mold at a pressure of 70–80 MPa to form cylindrical test samples with 7 mm in diameter, 12 mm in height, and a relative density of 60%. The relative density of the test specimen is related to the initial components. The theoretical density (ρTD) of the test specimen is calculated from the mass fraction (Y) and density (ρ) of each component through the following equation.

$$\frac{1}{\rho_{TD}} = \frac{Y_{Nb_2O_5}}{\rho_{Nb_2O_5}} + \frac{Y_{B_2O_3}}{\rho_{B_2O_3}} + \frac{Y_{Al}}{\rho_{Al}} + \frac{Y_{B}}{\rho_{B}} + \frac{Y_{MgO}}{\rho_{MgO}}$$

The SHS experiments were conducted in a windowed combustion chamber filled with high-purity (99.99%) argon. The propagation velocity of the combustion wave (Vₜ) was determined from the time sequence of recorded pictures. The reaction temperature was measured by the Pt/Pt-13%Rh bare wire thermocouple with a bead diameter of 125 μm. A thin ceramic (SiO₂) coating is usually to prevent the catalytic effect on the thermocouple in the measurement of gas-phase flame temperature of a combustion mixture involving hydrogen, methane, or propane as the fuel. Because solid-state combustion with argon as the surrounding gas is under investigation, the thermocouple without an inert coating was used by this work. Details of the experimental setup and scheme were described elsewhere [25,31]. After the SHS process, phase constituents of the products were analyzed by an X-ray diffractometer (Bruker D2, Billerica, MA, US) using CuKα radiation. The microstructure of the final product was examined by a scanning electron microscope (Hitachi S3000H, Tokyo, Japan) and elemental proportion was deduced from the energy dispersive spectroscopy (EDS). For Vickers hardness (Hᵥ) and fracture toughness (Kᵥc) measurement, selected experiments with the reactant compact placing in a steel mold were conducted. Upon the completion of the self-sustaining combustion reaction, densification of the product was carried out by a hydraulic press machine [25].
3. Results and Discussion

3.1. Combustion Wave Kinetics and Reaction Temperature

Figure 1 illustrates a typical series of combustion images obtained by this study, which was recorded from the powder compact of Reaction (2) with $y = 1.4$. As can be seen in Figure 1, a well-defined combustion wave is established upon ignition and propagates throughout the entire sample in a self-sustaining manner. This demonstrates sufficient reaction exothermicity of the reactant mixture. After combustion, the burned sample essentially retained its original shape.

![Typical sequence of self-sustaining combustion images recorded from Reaction (2) with $y = 1.4$.](image)

Figure 1. Typical sequence of self-sustaining combustion images recorded from Reaction (2) with $y = 1.4$.

The influence of the stoichiometric coefficient and excess boron on the flame-front velocity of Reactions (1) and (2) is presented in Figure 2. It was found that for the samples without excess boron, the combustion wave velocity of Reaction (1) increased from 2.5 to 6.6 mm/s with $x$ increasing from 0.6 to 1.0, while that of Reaction (2) decreased from 8.4 to 4.8 mm/s with $y$ in the range from 1.2 to 1.8. To be presented lately, it is believed that the variation of combustion front velocity with the reaction stoichiometry depends mainly on the exothermicity of the SHS process. As also indicated in Figure 2, samples with excess boron of 30 atom.% exhibit lower combustion wave speeds when compared to those without additional boron. This could be attributable to a prolonged sequence of phase evolution of borides in response to the increase of boron.

![Effects of NbB$_2$/MgAl$_2$O$_4$ ratio and excess boron on flame-front propagation velocity of Reactions (1) and (2).](image)

Figure 2. Effects of NbB$_2$/MgAl$_2$O$_4$ ratio and excess boron on flame-front propagation velocity of Reactions (1) and (2).

Figure 3 plots several measured sample temperature profiles, which depict a sharp rise signifying the rapid arrival of the combustion wave and a peak value corresponding to the combustion front temperature ($T_c$). After the progression of the combustion wave, a substantial temperature decline is a consequence of heat loss to the surroundings. As revealed in Figure 3, the peak temperature...
(\(T_c = 1516 \, ^\circ C\)) of Reaction (1) with \(x = 0.9\) is higher than that of \(x = 0.6\) \((T_c = 1317 \, ^\circ C)\) and the combustion front temperature of Reaction (2) decreases from 1606 \(^\circ C\) to 1416 \(^\circ C\) with an increase of \(y\) from 1.2 to 1.8. Based on the experimental measurement, the stoichiometric dependence of the combustion wave temperature is in agreement with that of flame-front velocity.

A comparison between the calculated adiabatic temperature and measured combustion front temperature of Reactions (1) and (2) is presented in Figure 4, indicative of a consistent variation of \(T_{ad}\) and \(T_c\) with the reaction stoichiometry. The increase of the combustion temperature of Reaction (1) with increasing \(\text{NbB}_2/\text{MgAl}_2\text{O}_4\) ratio is ascribed to a larger proportion of \(\text{Nb}_2\text{O}_5\) to \(\text{B}_2\text{O}_3\) in the thermite mixture, since the aluminothermic reduction of \(\text{Nb}_2\text{O}_5\) is more exothermic. However, a decline of the combustion temperature of Reaction (2) with \(\text{NbB}_2/\text{MgAl}_2\text{O}_4\) molar ratio confirms the cooling effect on combustion by increasing Nb and B because the elemental reaction of Nb with B is less energetic than the thermite reaction of \(\text{Nb}_2\text{O}_5\) and Al. As shown in Figure 4, the values of \(T_{ad}\) are higher by about 350–400 \(^\circ C\) than those of \(T_c\). The discrepancy between \(T_c\) and \(T_{ad}\) might result from considerable heat loss mostly by radiation, substantial boron elimination from the reaction zone, and formation of boride phases different from the stoichiometric composition.

![Figure 3](image-url)  
**Figure 3.** Combustion temperature profiles measured from samples of Reactions (1) and (2) with different stoichiometric coefficients.

![Figure 4](image-url)  
**Figure 4.** Calculated adiabatic temperatures and measured combustion temperatures of Reactions (1) and (2) as a function of the \(\text{NbB}_2/\text{MgAl}_2\text{O}_4\) molar ratio.
The activation energy ($E_a$) of solid-state combustion was deduced from combustion wave kinetics by constructing a correlation between $\ln(V/T_c)^2$ and $1/T_c$ in a form of linear relationship \cite{32,33}. Figure 5 depicts two sets of experimental data with best-fitted straight lines. From the slopes of straight lines, $E_a = 219.5 \pm 16$ and $167.9 \pm 13$ kJ/mol were deduced for Reactions (1) and (2), respectively. A larger $E_a$ for Reaction (1) means a higher kinetic barrier in comparison to Reaction (2). This could be caused most likely by the fact that the co-reduction of Nb$_2$O$_5$ and B$_2$O$_3$ by Al is required in Reaction (1) for the synthesis sequence to proceed, but Reaction (2) has only Nb$_2$O$_5$ to be reduced. According to Arrhenius kinetics, the activation energy of the solid-state reaction is governed by the reaction mechanism. In this study, aluminothermic reduction of metal oxides is considered as a first step of the SHS process, which is followed by a combination of Al$_2$O$_3$ and MgO to form MgAl$_2$O$_4$ and elemental interactions between Nb and B to produce NbB$_2$.

Figure 5. Correlation between combustion wave velocity and temperature for determination of activation energies ($E_a$) of Reactions (1) and (2).

3.2. Phase Composition and Microstructure of As-Synthesized Products

Figure 6a–c displays the XRD patterns of SHS-derived products from Reaction (1) of $x = 1.0$ without and with excess boron. As shown in Figure 6a, MgAl$_2$O$_4$ is identified and niobium borides exist in three phases including NbB$_2$, Nb$_3$B$_4$, and NbB. The formation of MgAl$_2$O$_4$ confirms a combination reaction between pre-added MgO and thermite-produced Al$_2$O$_3$. The presence of NbB and Nb$_3$B$_4$ denotes that the amount of boron is inadequate to transform all the borides into NbB$_2$. For the sample without extra boron, as shown in Figure 6a, NbB is the dominant boride phase. Besides, there is NbO$_2$ detected in the final product, indicative of an incomplete reduction of Nb$_2$O$_5$. For the sample with excess boron of 20 atom.%, Figure 6b indicates that the yield of Nb$_3$B$_4$ and NbB$_2$ is enhanced and NbO$_2$ is no longer detectable. Furthermore, Figure 6c reveals that more NbB$_2$ is formed in the final product obtained from the sample with extra boron of 30 atom.%. Although NbB$_2$ is the dominant boride in Figure 6c, the other two borides, NbB and Nb$_3$B$_4$, are not trivial. This means a substantial boron loss from the samples of Reaction (1) possibly through two different paths. One is the reduction of B$_2$O$_3$ and the other is the borothermal reaction between Nb$_2$O$_5$ and boron. Both reactions could generate gaseous B$_2$O$_2$ and BO, and they might expel from the sample compact.

The effect of excess boron on the formation of borides for Reaction (2) is presented in Figure 7a–c. Likewise, excess boron enhanced the production of NbB$_2$. It was found that the improvement is more effective for Reaction (2) than Reaction (1). Figure 7b unveils that NbB$_2$ prevails over NbB and Nb$_3$B$_4$ for the sample with excess boron of 20 atom.%. Moreover, as shown in Figure 7c, NbB and Nb$_3$B$_4$ become negligible in the resulting product from the sample with excess boron of 30 atom.%. This is because Reaction (2) contains no B$_2$O$_3$, only borothermal reduction of Nb$_2$O$_5$ could result in the loss of boron.
Figure 6. XRD patterns of NbB$_2$–MgAl$_2$O$_4$ composites synthesized from Reaction (1) of $x = 1.0$ under conditions: (a) without extra boron, (b) with extra boron 20%, and (c) with extra boron 30%.

Figure 7. XRD patterns of NbB$_2$–MgAl$_2$O$_4$ composites synthesized from Reaction (2) of $y = 1.6$ under conditions: (a) without extra boron, (b) with extra boron 20%, and (c) with extra boron 30%.

Typical microstructures of the fracture surface of the NbB$_2$–MgAl$_2$O$_4$ composites synthesized from Reactions (1) and (2) with 30 atom.% extra boron are illustrated in Figure 8a,b, respectively.
As displayed in the micrographs of Figure 8a,b; the long rod-shaped MgAl₂O₄ crystals form a dense matrix with an interlocking structure and small NbB₂ grains are embedded in MgAl₂O₄ or distributed over the surface. Furthermore, MgAl₂O₄ and NbB₂ phases in Figure 8a are confirmed by the atomic ratios of Mg:Al:O = 14.1:28.9:57.0 and Nb:B = 32.7:67.3 deduced from the EDS spectrum. Similarly, in Figure 8b, MgAl₂O₄ and NbB₂ are determined to have Mg:Al:O = 13.7:29.8:56.5 and Nb:B = 33.1:66.9, both of which match well with their exact stoichiometries.

Figure 8. SEM micrographs and EDS spectra of NbB₂–MgAl₂O₄ composites of (a) Reaction (1) of x = 1.0 with 30 atom.% excess boron and (b) Reaction (2) of y = 1.6 with 30 atom.% excess boron.

Densified products have a relative density of about 92%–95%. For the NbB₂–MgAl₂O₄ composite synthesized from Reaction (1) of x = 1.0, \( H_v = 15.2 \) GPa and \( K_{IC} = 4.82 \) MPa m\(^{1/2} \) were determined. The composite obtained from Reaction (2) of y = 1.8 exhibits \( H_v = 16.9 \) GPa and \( K_{IC} = 4.37 \) MPa m\(^{1/2} \). When compared with pure NbB₂ \((K_{IC} = 3.76 \) MPa m\(^{1/2} \)) [34], the NbB₂–MgAl₂O₄ composite is toughened. Similar materials like TiB₂–Al₂O₃ composites fabricated by hot pressing at a sintering temperature of 1700 °C showed a relative density of about 96.2%, Vickers hardness of 24.8 GPa, and fracture toughness of 4.56 MPa m\(^{1/2} \) [35]. This confirms that satisfactory toughness is obtained for the NbB₂–MgAl₂O₄ composite synthesized by this study.
4. Conclusions

This study prepared NbB₂–MgAl₂O₄ in situ composites with a molar ratio of NbB₂/MgAl₂O₄ from 0.6 to 1.8 by the SHS process with reducing stages. Within the scope of experimental variables, combustion front velocity and temperature increased with NbB₂ content for Reaction (1), because the proportion of Nb₂O₃ to B₂O₃ in the thermite mixture increased. On the other hand, Reaction (2) showed a decrease in combustion velocity and temperature as NbB₂ content increased, because of the dilution effect of additional Nb and B on combustion. The activation energies, \( E_a = 219.5 \pm 16 \) and \( 167.9 \pm 13 \) kJ/mol, were, respectively, deduced for Reactions (1) and (2), suggesting a higher kinetic barrier for Reaction (1).

The XRD analysis of the final product confirms the formation of MgAl₂O₄ from thermite-produced Al₂O₃ and pre-added MgO. For the samples without extra boron, three boride phases, NbB, Nb₃B₄, and NbB₂, were formed and dominated by NbB. Excess boron up to 30 atom.% effectively compensated for the loss of boron during combustion and promoted the formation of NbB₂ as the major boride compound. The microstructure of as-synthesized NbB₂–MgAl₂O₄ composites is characterized by interlocking rod-shaped MgAl₂O₄ crystals and small NbB₂ grains embedded in MgAl₂O₄ or distributed over the surface. Fracture toughness of the NbB₂–MgAl₂O₄ composite was improved up to \( K_{IC} = 4.37\text{–}4.82 \) MPa m\(^{1/2}\).

Author Contributions: Conceptualization, C.-L.Y. and Y.-C.C.; methodology, C.-L.Y. and Y.-C.C.; validation, C.-L.Y. and Y.-C.C.; formal analysis, C.-L.Y. and Y.-C.C.; investigation, C.-L.Y. and Y.-C.C.; resources, C.-L.Y.; data curation, C.-L.Y. and Y.-C.C.; writing—original draft preparation, C.-L.Y. and Y.-C.C.; writing—review and editing, C.-L.Y. and Y.-C.C.; supervision, C.-L.Y.; project administration, C.-L.Y.; funding acquisition, C.-L.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research work was funded by the Ministry of Science and Technology of Taiwan under the grant of MOST 108-2221-E-035-026.

Acknowledgments: Authors are thankful for Precision Instrument Support Center of Feng Chia University in providing materials analytical facilities.

Conflicts of Interest: The authors declare no conflicts of interest.

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