Direct Copolymerization of CO\(_2\) and Diols

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Direct polymerization of CO\(_2\) and diols is promising as a simple and environmental-benign method in place of conventional processes using high-cost and/or hazardous reagents such as phosgene, carbon monoxide and epoxides, however, there are no reports on the direct method due to the inertness of CO\(_2\) and severe equilibrium limitation of the reaction. Herein, we firstly substantiate the direct copolymerization of CO\(_2\) and diols using CeO\(_2\) catalyst and 2-cyanopyridine promotor, providing the alternating cooligomers in high diol-based yield (up to 99%) and selectivity (up to >99%). This catalyst system is applicable to various diols including linear C\(_4\)–C\(_{10}\) \(\alpha,\omega\)-diols to provide high yields of the corresponding cooligomers, which cannot be obtained by well-known methods such as copolymerization of CO\(_2\) and cyclic ethers and ring-opening polymerization of cyclic carbonates. This process provides us a facile synthesis method for versatile polycarbonates from various diols and CO\(_2\) owing to simplicity of diols modification.

Direct transformation of CO\(_2\) to valuable chemicals is one of the hottest topics from the viewpoints of environmental and green chemistry\(^1\)–\(^7\). Transformation of CO\(_2\) can be mainly categorized into two methods, reductive transformation and non-reductive transformation\(^8\)–\(^11\). The non-reductive transformation of CO\(_2\) comprises the reactions of CO\(_2\) with compounds having polar functional groups such as alcohols and amines, providing various important chemicals such as ureas, carbamates, carbonates and polycarbonates, and it is promising because of lower energy input compared with the reductive transformation. However, since CO\(_2\) is very stable owing to the very strong double bond, an exquisite catalyst system to activate CO\(_2\) and reagents is essential. Carbonic anhydrase is well-known as an ideal catalyst system for non-reductive transformation of CO\(_2\), drastically accelerating the reaction of CO\(_2\) and H\(_2\)O to bicarbonate and proton (~10\(^6\)-fold vs non-catalyst)\(^8\)–\(^12\). In this catalyst system, Zn\(^{2+}\) ion and a histidine residue activate H\(_2\)O to generate reactive hydroxide species on Zn\(^{2+}\) ion (cooperation of Lewis acid and Lewis base), and CO\(_2\) is guided near the hydroxide species by the hydrophobic pocket composed of three valine residues (substrate concentration), forming a configuration that is conductive to reaction. As for artificial catalysts, achieving the sufficient level comparable to enzymes is quite difficult due to the smaller size of the artificial catalysts than enzymes. Therefore, it is desirable to create exquisite and precise artificial catalysts that can simultaneously activate CO\(_2\) and reagents in proximity of each other.

CeO\(_2\) has been widely used in the fields of catalyst and biological chemistry because of its unique acid-base and redox properties\(^13\)–\(^14\), and has recently attracted much attention in liquid-phase organic syntheses at low temperature (\(\leq 473\) K)\(^15\)–\(^21\). In particular, it has been reported that CeO\(_2\) plays a crucial role in the catalytic non-reductive conversion of CO\(_2\) to organic carbonates, carbamates and ureas using alcohols or amines\(^22\)–\(^32\), although these reactions have a common problem of the equilibrium limitation. Recently, we found that CeO\(_2\)-catalyzed dehydroxylation condensation of alcohols and CO\(_2\) in combination with CeO\(_2\)-catalyzed hydration of 2-cyanopyridine to picolinamide enabled the formation of the corresponding organic carbonates in high yields\(^33\)–\(^35\). The methanol-based yield of DMC in the reaction of CH\(_3\)OH, CO\(_2\) and 2-cyanopyridine reached 94% yield, while the equilibrium yield of DMC is below 1% in the reaction of CH\(_3\)OH and CO\(_2\) without 2-cyanopyridine. This is the first report on stoichiometric transformation of alcohols with CO\(_2\) to the corresponding carbonate. We also demonstrated that CO\(_2\) can be strongly adsorbed and activated on acid-base sites of CeO\(_2\)\(^36\)–\(^38\) and that methanol can be activated cooperatively by both CeO\(_2\) and 2-cyanopyridine at the interface between CeO\(_2\) and 2-cyanopyridine\(^39\), which has something common to the above enzyme catalyst system (mainly cooperation of Lewis acid and Lewis base, and co-promoter).

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and substrate concentration). In addition, Urakawa and co-workers also applied this catalyst system to the DMC synthesis under a wide range of CO2 pressure (1–30 MPa) in a fixed bed reactor, achieving higher reaction rates than that in batch operation37. These results inspired us to apply this catalyst system to the direct synthesis of polycarbonates from CO2 and diols.

Polycarbonates has been commonly used as an engineering plastic, and the market size is 290 million ton/year in 2009 and expected to increase on average by about 4 ~ 6% each year to 202038,39. Therefore, the polycarbonates are one of the most promising targets from CO2, which will contribute to the incorporation of large amount of CO2 into chemicals due to the large market size. Polycarbonates have been industrially produced by using phosgene as a carbonyl source, however, phosgene is highly toxic, and the process gives rise to a large amount of salts by neutralization. To overcome these drawbacks, processes using organic carbonates as a carbonyl source have been developed such as condensation of diols and organic carbonates40–42 and ring-opening polymerization of cyclic carbonates43–47 (Fig. 1). However, these processes have similar problems to the phosgene process because the organic carbonate substrates in these processes have been usually synthesized by the reaction of phosgene with the corresponding alcohols or epoxides, and an alternative environmental-benign synthesis process of the organic carbonates have not been established. As for processes using CO2 as a carbonyl source, copolymerization of cyclic ethers and CO2 have been intensively investigated (Fig. 1) (selected reviews48–51 and selected recent papers52–64). Epoxides and oxetanes have been used as starting materials; however the copolymerization of CO2 and cyclic ethers with five-membered or larger ring has not been reported at all because such cyclic ethers are difficult to be prepared due to the low stability. On the other hand, the direct polymerization of diols and CO2 by dehydration condensation will enable the synthesis of polycarbonates containing longer alkyl chains (Fig. 1, this work). However, the dehydration condensation of diols and CO2 is seriously limited by the reaction equilibrium. For example, it is well-known that the equilibrium yield of propylene carbonate from 1,2-propanediol and CO2 on 1,2-propanediol basis has been estimated to be below 2%65. Regarding the direct synthesis of polycarbonates from α,ω-diols and CO2, to the best of our knowledge, there are no reports on catalytic and non-catalytic synthesis methods, although conversion of CO2, diols and dihalides to polycarbonates using K2CO3 was reported66.

Herein, we demonstrate that the combination of CeO2 catalyst and 2-cyanopyridine promoter is effective for the direct copolymerization of diols and CO2. This is a first report on the catalytic direct synthesis of cooligomers from CO2 and diols.

Results

Catalyst screening. First, the polymerization from CO2 and 1,4-butanediol was investigated using various metal oxides with 2-cyanopyridine (Table 1). 2-Cyanopyridine was selected as a dehydrating agent because 2-cyanopyridine is preferable for the hydration over CeO233–35,67,68. The reaction was carried out with an autoclave reactor containing a metal oxide (0.17 g), 1,4-butanediol (10 mmol), 2-cyanopyridine (100 mmol) and CO2 (5.0 MPa) at 403 K. Conversion and selectivity were calculated on the 1,4-butanediol basis. The detailed data for conversion of 2-cyanopyridine are shown in Supplementary Table S1. No oligomer product was obtained without a metal oxide catalyst (Table 1, entry 13). CeO2 provided the oligomer in 97% yield (Mn = 1070, dispersity

Figure 1. Synthesis methods of polycarbonates.
\((M_w/M_n) = 1.33\) with slight amount of 4-hydroxybutyl picolinate, which was produced by 2-cyanopyridine and 1,4-butanediol (Table 1, entry 1), and the \(M_n\) of the oligomer corresponds to the oligomers formed from eight \(\text{CO}_2\) and eight 1,4-butanediol. MALDI-TOF mass spectroscopy revealed the formation of the alternating cooligomer from \(\text{CO}_2\) and 1,4-butanediol (Fig. 2), and confirmed no formation of the ether bond. In addition, 2-picolinamide was produced selectively by reaction of 2-cyanopyridine with \(\text{H}_2\text{O}\) that is produced by the copolymerization from \(\text{CO}_2\) and 1,4-butanediol (Supplementary Table S1). On the other hand, other metal oxides showed lower conversion than \(\text{CeO}_2\) and gave no oligomers (Table 1, entries 3–12). Others would include dimer, trimer or diester produced from 2-cyanopyridine and 1,4-butanediol. Therefore, among the metal oxides tested, \(\text{CeO}_2\) is the only active metal oxide for the reaction by using 2-cyanopyridine as a dehydrating agent. It should be noted that \(\text{CeO}_2\)

**Table 1. Direct copolymerization of 1,4-butanediol and \(\text{CO}_2\) using a metal oxide catalyst and 2-cyanopyridine.**

*Reaction conditions: metal oxide 0.17 g, 1,4-butanediol 10 mmol, 2-cyanopyridine 100 mmol, \(\text{CO}_2\) 5 MPa (at r.t.), 403 K, 8 h. *Based on crude sample, polystyrene equivalent molar mass (\(M_n\)(SEC)). †Dispersity is an index (\(M_w/M_n\)) determined by SEC with THF as eluent. §Second use.

**Figure 2. MALDI-TOF mass spectrum of the products from \(\text{CO}_2\) and 1,4-butanediol using \(\text{CeO}_2\) and 2-cyanopyridine.**
CO₂ 0.5–5 MPa (at r.t.), 403 K, 8 h. †Based on crude sample, polystyrene equivalent molar mass (Mₚ).

The attack of the OH group at the end of polymer, which is known as back-biting.

Dispersity are attributed to degradation of the oligomers and/or intramolecular termination by the nucleophilic attack of the OH group.

We first demonstrated direct copolymerization from CO₂ and 1,4-butanediol using the combination of CeO₂ catalyst and 2-cyanopyridine promoter. In addition, the reusability of CeO₂ catalyst was investigated. CeO₂ was easily retrieved from the reaction mixture by decantation, and the collected catalyst was washed with methanol, followed by calcining at 873 K for 3 h, and then the recovered CeO₂ was used for the next reaction. CeO₂ could be reused without remarkable loss of activity and selectivity. XRD and BET analyses confirmed that the structure of CeO₂ was unchanged during the reusability test. In addition, the dissolved amount of Ce species in the filtrate was below the detection level (0.1 %) of ICP-AES, which indicates that CeO₂ worked as a truly heterogeneous catalyst in this reaction.

| Entry | 2-Cyanopyridine [mmol] | Conversion [%] | Selectivity (%) | Mₚ [g mol⁻¹] | Dispersity |
|-------|------------------------|----------------|-----------------|--------------|-----------|
|       |                        |                | Oligomer        | 4-Hydroxybutyl | Others    |           |
| 1     | 5                      | 68             | 99              | 1            | <1        | 510       | 1.14     |
| 2     | 10                     | 93             | 98              | 2            | <1        | 910       | 1.37     |
| 3     | 20                     | 98             | 98              | 2            | <1        | 1110      | 1.34     |
| 4     | 50                     | 99             | 98              | 2            | <1        | 1030      | 1.32     |
| 5     | 100                    | 99             | 97              | 4            | <1        | 1070      | 1.33     |
| 6     | 200                    | 99             | 97              | 3            | <1        | 900       | 1.33     |

Table 2. Effect of 2-cyanopyridine amount on the polymerization of 1,4-butanediol and CO₂ using CeO₂ catalyst. Conditions: CeO₂ 0.17 g, 1,4-butanediol 10 mmol, 2-cyanopyridine 5–200 mmol, CO₂ 5 MPa (at r.t.), 403 K, 8 h. †Based on crude sample, polystyrene equivalent molar mass (Mₚ (SEC)). ‡Dispersity is an index (Mₚ/Mₙ) determined by SEC with THF as eluent.

| Entry | CO₂ pressure | Conversion [%] | Selectivity (%) | Mₚ [g mol⁻¹] | Dispersity |
|-------|--------------|----------------|-----------------|--------------|-----------|
|       |              |                | Oligomer        | 4-Hydroxybutyl | Others    |           |
| 1     | 0.5          | 88             | 99              | 1            | <1        | 630       | 1.24     |
| 2     | 1            | 93             | 99              | 1            | <1        | 700       | 1.29     |
| 3     | 2            | 96             | 99              | 1            | <1        | 790       | 1.31     |
| 4     | 3            | 98             | 99              | 1            | <1        | 900       | 1.32     |
| 5     | 5            | 99             | 97              | 3            | <1        | 1070      | 1.33     |

Table 3. Effect of CO₂ pressure on the polymerization of 1,4-butanediol and CO₂ using CeO₂ catalyst and 2-cyanopyridine. Reaction conditions: CeO₂ 0.17 g, 1,4-butanediol 10 mmol, 2-cyanopyridine 100 mmol, CO₂ 0.5–5 MPa (at r.t.), 403 K, 8 h. †Based on crude sample, polystyrene equivalent molar mass (Mₚ (SEC)). ‡Dispersity = polydispersity index (Mₚ/Mₙ) determined by SEC with THF as eluent.

Performance of combination of CeO₂ catalyst and 2-cyanopyridine promoter. 2-Cyanopyridine reacts with one mole of H₂O to provide 2-picolinamide, indicating that 10 mmol of 2-cyanopyridine is theoretically necessary to convert all of 1,4-butanediol to the corresponding oligomer when 10 mmol of 1,4-butanediol is used. Effect of 2-cyanopyridine amount was studied using CeO₂ catalyst (Table 2, the detailed data for conversion of 2-cyanopyridine are shown in Supplementary Table S2). 10 mmol and larger than 10 mmol of 2-cyanopyridine provided almost the same conversion and Mₚ (Table 2, entries 2–6), although 5 mmol of 2-cyanopyridine is not effective due to the smaller amount of 2-cyanopyridine than the theoretical amount (Table 2, entry 1). Therefore, the equivalent amount of 2-cyanopyridine is enough for the formation of the oligomer from 1,4-butanediol and CO₂.

Low CO₂ pressure is preferable from the environmental and economic viewpoints. The effect of CO₂ pressure was investigated using CeO₂ catalyst and 2-cyanopyridine promoter (Table 3, the detailed data for conversion of 2-cyanopyridine are shown in Supplementary Table S3). The reaction proceeds even at low CO₂ pressure of 0.5 MPa to give the oligomer in good yield (Table 3, entry 1), although the conversion and Mₚ gradually decreased with decreasing CO₂ pressure. This result provides the possibility to perform the reaction at low CO₂ pressure.

The time-course of the copolymerization of CO₂ and 1,4-butanediol was investigated using CeO₂ catalyst and 2-cyanopyridine promoter (Fig. 3, the detailed data are shown in Supplementary Table S4 and Supplementary Figs S2 and S3). The reaction rapidly proceeded to reach 99% conversion in one hour, and the high selectivity to the oligomer (≥97%) was maintained from the short reaction time, which strongly indicates that the oligomers were not produced via formation of tetramethylene carbonate, the corresponding cyclic carbonate. On the other hand, the Mₚ increased with the reaction time up to 8 h, but decreased gradually at more than 8 h. Dispersity also increased to about 1.3 in one hour and gradually increased at more than 1 h. The decrease of Mₚ and increase of dispersity are attributed to degradation of the oligomers and/or intramolecular termination by the nucleophilic attack of the OH group at the end of polymer, which is known as back-biting.
Finally, the scope of diols was investigated in the copolymerization of CO$_2$ and diols using CeO$_2$ catalyst and 2-cyanopyridine (Table 4, the detailed data for conversion of 2-cyanopyridine are shown in Supplementary Table S5). Linear C$_4$–C$_{10}$ $\alpha$,$\omega$-diols were converted to the corresponding cooligomers in good yields. The corresponding cyclic carbonates were not also observed in the case of C$_5$–C$_{10}$ diols, which supports that the direct dehydration condensation of diols and CO$_2$ takes place in this reaction system. The average number of the repeating unit of these copolymers was 7 ~ 8 even with any diols. 1,4-Cyclohexanedimethanol and 1,4-benzenedimethanol, which are diols with rigid structure, were converted to the corresponding copolymers, however, the reactivity and $M_n$ were lower than those of linear alkyl diols. To examine the effect of the position of the OH group, the combination of CeO$_2$ catalyst and 2-cyanopyridine promoter was applied to 1,5-hexanediol.
having one primary and one secondary OH groups, 2,5-hexanediol having two secondary OH groups, and 2,5-dimethyl-2,5-hexanediol having two tertiary OH groups. 1,5-Hexanediol showed lower conversion, selectivity and $M_n$ than 1,6-hexanediol having two primary OH groups. 2,5-Hexanediol showed further lower conversion, selectivity and $M_n$ than 1,5-hexanediol. In the case of 2,5-dimethyl-2,5-hexanediol, the corresponding oligomer was not obtained. Therefore, steric hindrance around the OH group drastically decreases the substrate reactivity.

Proposed reaction mechanism. The proposed reaction mechanism is shown in Fig. 4. Based on the previous reports on carbonate synthesis from alcohol and CO$_2$ over CeO$_2$ catalyst$^{35}$, the reaction starts with (i) adsorption of diol on CeO$_2$ surface to form alkoxide adspecies. (ii) CO$_2$ insertion to the some alkoxide adspecies, providing some carbonate adspecies. (iii) Nucleophilic attack of the oxygen anion in the alkoxide adspecies to the carbonate adspecies to afford the corresponding carbonate from 1,4-butanediol and H$_2$O. (iv) Removal of the produced H$_2$O by hydration of 2-cyanopyridine to 2-picolinamide over CeO$_2$.$^{33–35,67}$ (v) Finally, further reaction of the produced carbonate with CO$_2$, 1,4-butanediol or produced cooligomer, giving polytetramethylene carbonate. Among these reaction steps, the step (iv) is very important in the polycarbonate synthesis, which will drastically shift the reaction to the product side by removal of H$_2$O from the reaction media.

Discussion

In summary, we first demonstrated the direct copolymerization from CO$_2$ and diols using the combination of CeO$_2$ catalyst and 2-cyanopyridine promoter. Various diols including $\alpha,\omega$-diols with long alkyl chain can be transformed to the corresponding cooligomers, which cannot be obtained by the conventional methods with cyclic carbonate, epoxides or oxetanes. This catalyst system will not only open up a new epoch for polymer chemistry, particularly polycarbonate synthesis, but also make a large impact on transformation of CO$_2$.

Methods

Materials. Preparation of CeO$_2$ catalyst was carried out by calcining CeO$_2$-HS (Daichi Kigenso, Japan. The purity of CeO$_2$: 99.97%) for 3 h in air at 873 K. The specific surface area (BET method) of the CeO$_2$ was 84 m$^2$/g. All the chemicals for organic reactions were commercially available and were used without further purification. Other metal oxides were commercially available or synthesized by the precipitation method: ZrO$_2$ (Daichi Kigenso Kogyo Co. Ltd., Zr(OH)$_4$ was calcined under air at 873 K for 3 h.), MgO (Ube Industries, Ltd., MgO 500A, 873 K, 3 h), TiO$_2$ (Nippon Aerosil Co. Ltd., P-25), $\gamma$-Al$_2$O$_3$ (Nippon Aerosil), ZnO (FINEX-50, Sakai Chemical Industry Co., Ltd), SiO$_2$ (Fuji Silysia Chemical Ltd., 773 K, 1 h), Nb$_2$O$_5$ (Companhia Brasileira de Metalurgia e Mineracao (CBMM), Nb$_2$O$_5$·nH$_2$O was calcined at 773 K for 3 h). Y$_2$O$_3$, La$_2$O$_3$ and Pr$_6$O$_{11}$ were prepared by the precipitation method. Y(NO$_3$)$_3$·nH$_2$O (Wako Pure Chemical Industries Ltd., $>99.9\%$), La(NO$_3$)$_3$·6H$_2$O (Wako Pure Chemical Industries Ltd., $>99.9\%$) and Pr(NO$_3$)$_3$·nH$_2$O (Wako Pure Chemical Industries Ltd., $>99.5\%$) were used as precursors. A precursor (25 g) was dissolved in water (100 ml) and NH$_3$aq (1 M) was dropped with stirring until the pH of the solution became 10, resulting in a precipitate. The precipitate was filtered and washed by water, followed by drying at 383 K overnight (12 h) and calcining under air at 873 K (673 K for La$_2$O$_3$) for 3 h.

Typical procedure for direct polymerization of CO$_2$ and 1,4-butanediol. All the reactions were carried out in an autoclave reactor with an inner volume of 190 mL. The standard procedure of direct polymerization of CO$_2$ and 1,4-butanediol using the combination catalyst of CeO$_2$ and 2-cyanopyridine was as follows: CeO$_2$ (0.17 g, 1 mmol), 1,4-butanediol 0.90 g (10 mmol) and 2-cyanopyridine 10.4 g (100 mmol) were put into the autoclave together with a spinner, and then the reactor was purged with 1 MPa CO$_2$ (Shimakyo Co. Ltd., $>99.5\%$) three times. The autoclave was pressurized with CO$_2$ to the desired pressure (typically 5.0 MPa) at room
temperature, and then the autoclave was heated to 433 K, where the CO$_2$ pressure was about 12 MPa. The mixture was constantly stirred during the reaction. After the reaction time, the reactor was cooled in water bath to room temperature. THF (20 ml) was added to the liquid phase as a solvent, and 1-hexanol (~0.2 ml) was also added as an internal standard substance for a quantitative analysis. The reactor was washed with THF, and the liquids used in washing were added to the reaction mixture. Amount of 2-cyanopyridine and products from 2-cyanopyridine such as 2-picolinamide and 4-hydroxybutyl picolinate were analyzed by gas chromatography (Shimadzu GC-2014) equipped with an FID using a CP/Sil 5 CB. Since produced cooligomers is decomposed by heating, the amount of 1,4-butanediol was analyzed by HPLC (Shimazu Prominence) equipped with an RI detector (RID-10A) using a Phenyl-Hexyl Luna column ( Phenomenex, particle size 5 μm, 250 mm × 4.6 mm, conditions: developing solvent, H$_2$O/CH$_3$OH = 70/30, 0.5 ml/min, 313 K). Since produced cooligomers were precipitated by addition of the developing solvent (about 20-fold dilution), the precipitated cooligomers were removed by filtration before analyzing by HPLC. This filtration operation was conducted at least two times until the precipitation was not observed. The qualitative analysis of the products were conducted by a gas chromatograph equipped with a quadrupole mass spectrometer (GC-MS, Shimazu QP5050) using the same capillary columns and NMR (Bruker, AV400). The oligomerized products were analyzed by MALDI-TOF mass (Shimazu AXIMA-CFR Plus) using dithranol and NaBr as a matrix and ionization agent, respectively, and size exclusion chromatography (SEC, Shimazu Prominence) with a RI detector (RID-10A) using a Shodex HPLC column KF-805L. The developing solvent is THF (Wako Pure Chemical Industries, >99.5%).

Catalyst characterization. The surface area of CeO$_2$ was measured with BET method (N$_2$ adsorption) using Gemini (Micromeritics). X-ray diffraction (XRD) patterns were recorded using MiniFlex 600 with Cu Kα (40 kV, 15 mA) radiation. The amount of eluted metal into the reaction solution was analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher Scientific iCAP 6500).

The conversion and selectivity were calculated by the following equations (Eqs 1–3).

\[
\text{Conversion}/\% = 100 \times \left[1 - \frac{\text{Amount of diol after reaction (mmol)}}{\text{Amount of diol before the reaction (mmol)}}\right]
\]

Eqs 1

\[
\text{Selectivity}/\% = 100 \times \frac{\left[\text{Amount of the product (mmol)}\right]}{\left[\text{number of diol units in the product (mmol)}\right]} \times \frac{\text{Amount of reacted diol (mmol)}}{\text{(Amount of reactant)}}
\]

Eqs 2

\[
\text{Yield}/\% = \text{Conversion}/\% \times \text{selectivity}/\% / 100
\]

The amount of oligomer was determined by subtraction of the amount of the produced ester from the amount of reacted diol. The products in which the signal was not observed by SEC were assigned to others.

Catalyst characterization. The surface area of CeO$_2$ was measured with BET method (N$_2$ adsorption) using Gemini (Micromeritics). X-ray diffraction (XRD) patterns were recorded using MiniFlex 600 with Cu Kα (40 kV, 15 mA) radiation. The amount of eluted metal into the reaction solution was analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher Scientific iCAP 6500).

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Author Contributions
M.T. and K.T. conceived the concept and directed the project. I.K., M.T. and H.M. conducted experiments. M.T., Y.N. and H.S. discussed the experiments and results, and prepared the manuscript.

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