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Zinc-glutarate (ZnGA) is a promising catalyst that can form polymers from CO₂ and epoxides, thereby contributing to the development of CO₂ utilization technologies and future sustainability. One of the obstacles to commercializing ZnGA in polymer industries is its low catalytic activity. In this study, we introduced activated two-dimensional (2D) ZnGA to improve its catalytic activity in polymerization. The morphology-controlled 2D ZnGA was treated with H₃Co(CN)₆, and a porous granular-type Co-modified ZnGA (Co-ZnGA) was prepared. The morphology of 2D ZnGA is a prerequisite for the activation by H₃Co(CN)₆. The catalytic properties of Co-ZnGA were evaluated by copolymerization of various epoxides and CO₂, and exhibited catalytic activity of 855, 1540, 1190, and 148 g g-cat⁻¹ with propylene oxide, 1,2-epoxyhexane, 1,2-epoxybutane, and styrene oxide, respectively. This study provided a new strategy using 2D ZnGA instead of conventional ZnGA for increasing the catalytic activity in CO₂ polymerization.

1. Introduction

Accumulation of CO₂ in the atmosphere because of the anthropogenic carbon cycle has increased environmental sustainability concerns, which include global warming and climate change. The catalytic conversion of CO₂ into industrially valuable chemicals to reduce CO₂ emissions has attracted interest.^{1,2} Valorisation of CO₂ into useful chemical products has importance in not only mitigating CO₂ levels but also utilizing a renewable, nontoxic, and low-cost C1 building block (CO₂) in the chemical industries. Among the various chemical conversions of CO₂, the polymerization of CO₂ and epoxides affording poly(alkylene carbonates) has the advantage of storing a large amount of CO₂ in the polymer (50 wt% of CO₂ in poly(ethylene carbonate)) and meeting the demand for high-performance biodegradable polycarbonates in the polymer industry.^{3–6}

Zinc glutarate (ZnGA) is a catalyst used to synthesize polycarbonates from CO₂ and epoxides.⁴ Despite economic advan-

tages and easy preparation of the catalyst from ZnO and glutaric acid, the industrial use of ZnGA is limited, due to its low catalytic activity.^{7–10} Substantial research has been undertaken on the improvement of catalytic activity of ZnGA, which concluded that structure and crystallinity are limiting factors.^{11,12} Zinc glutarate comprises Zn(II) ions linked to four glutarates, where two are angled and two are straight, thereby forming a three-dimensional network.^{13,14} The space inside the three-dimensional framework is insufficient for the diffusion of monomers, resulting in polymerization occurring only at the surface of the catalyst. Thus, the surface area of ZnGA was increased to improve catalytic activity, with surface etching and reduction in the size of ZnGA being reported.¹⁵ Another strategy is to increase the active zinc sites through surface modification (Fig. 1). For example, introducing ethylsulfinate, Lewis acid (MCl_n), or hydroxy groups to ZnGA, increased catalytic activity, which is likely due to the increased number of active zinc sites for polymerization.^{16–19} In this paper, we present a protocol for increasing the active zinc sites, the

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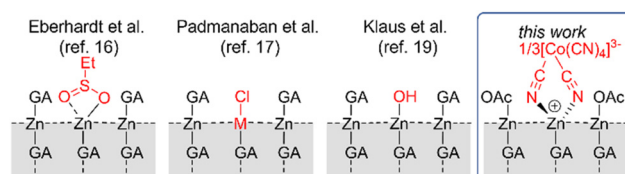


Fig. 1 Generation of active zinc sites using surface modification in previous studies compared to this study.

surface area, and porosity of ZnGA using the reaction of thin plate ZnGA (two-dimensional (2D) ZnGA) with $\text{H}_3\text{Co}(\text{CN})_6$. The synthesis and characterization of 2D ZnGA, the modification of 2D ZnGA by $\text{H}_3\text{Co}(\text{CN})_6$ to form Co-modified ZnGA (Co-ZnGA), and the polymerization results using Co-ZnGA are presented.

2. Results and discussion

The synthesis of 2D ZnGA and the surface activation of 2D ZnGA by the reaction with $\text{H}_3\text{Co}(\text{CN})_6$ are illustrated in Fig. 2. The 2D ZnGA was prepared by controlling the growth of ZnGA in acetic acid. The acetic acid competed with the glutaric acid during the reaction with ZnO, resulting in shape-controlled 2D ZnGA. The reaction of ZnO and glutaric acid without acetic acid formed conventional ZnGA.⁷ Because ZnX_2 (X = halogen or acid) reacts with $\text{H}_3\text{Co}(\text{CN})_6$ forming active $[\text{ZnX}]^+$ species,^{20,21} 2D ZnGA possessing acetate groups at the surface is susceptible to reacting with $\text{H}_3\text{Co}(\text{CN})_6$, thus forming monocationic zinc sites. The acetate ligands at the surface of 2D ZnGA were postulated to induce an acid-base reaction when combined with $\text{H}_3\text{Co}(\text{CN})_6$, forming monocationic Co-ZnGA (Fig. 2). The ratios of $\text{H}_3\text{Co}(\text{CN})_6$ and 2D ZnGA were adjusted between 1 : 2 and 1 : 4 for the synthesis of catalysts. The activity of Co-ZnGA catalysts was compared by polymerizing epoxides and CO_2 , and the physical properties of polymers formed by the Co-ZnGA catalysts are discussed. The characterization of 2D ZnGA and Co-ZnGA synthesized from $\text{H}_3\text{Co}(\text{CN})_6$ and 2D ZnGA at a ratio of 1 : 3 are presented below.

The morphologies of 2D ZnGA and Co-ZnGA were investigated using scanning electron microscopy (SEM) (Fig. 3). As shown in Fig. 3a, the SEM image of 2D ZnGA displays thin plate widths, lengths, and thicknesses of 320–800 nm, 600 nm–2.2 μm , and 35–45 nm, respectively. In comparison, the Co-ZnGA displayed granular morphology with a reduced size of 240–720 nm, indicating that the treatment of 2D ZnGA plates with $\text{H}_3\text{Co}(\text{CN})_6$ induced the cutting of the plates into smaller granules (Fig. 3b). The surface areas and porosity of materials were characterized by analyzing N_2 adsorption-desorption isotherm curves based on the Brunauer-Emmett-Teller (BET) theory (Fig. 3c). In the conversion of 2D ZnGA to

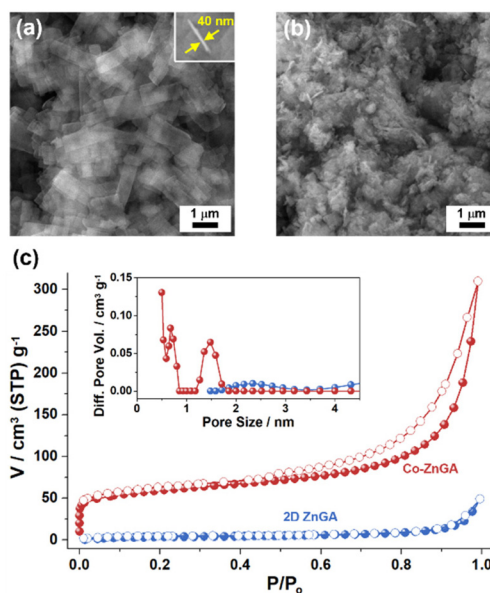


Fig. 3 SEM images of (a) 2D ZnGA and (b) Co-ZnGA. (c) N_2 adsorption-desorption isotherm curves obtained at 77 K, pore size distribution diagrams based on the DFT method (inset) of 2D ZnGA and Co-ZnGA.

Co-ZnGA, the surface areas and the porosity changed substantially. The surface area of 2D ZnGA was $15 \text{ m}^2 \text{ g}^{-1}$ with a poor pore volume of $0.03 \text{ cm}^3 \text{ g}^{-1}$, and that of Co-ZnGA was substantially increased to $215 \text{ m}^2 \text{ g}^{-1}$ and $0.28 \text{ cm}^3 \text{ g}^{-1}$, respectively (Fig. 3c). The surface area of 2D ZnGA ($15 \text{ m}^2 \text{ g}^{-1}$) is comparable to that of standard ZnGA ($15 \text{ m}^2 \text{ g}^{-1}$, see ESI, Fig. S1†). These observations indicate that many structural defects were formed in Co-ZnGA when treating 2D ZnGA with $\text{H}_3\text{Co}(\text{CN})_6$.

The chemical structures of ZnGA and Co-ZnGA were characterized using powder X-ray diffraction (PXRD), infrared absorption (IR), and solid-state CP-TOSS ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Fig. 4a–c). The PXRD pattern of 2D ZnGA displayed a main diffraction peak of 2θ at 12.2° , which is consistent with main diffraction peak observed in ZnGA in the literature (Fig. 4a).¹⁰ Due to its thin-plate morphology, the remaining ZnGA PXRD diffraction peaks in the 2D ZnGA weakened substantially.²² In comparison, the Co-ZnGA PXRD pattern displayed a significantly reduced main diffraction peak intensity of 2θ at 12.2° , indicating decreased crystalline domain sizes owing to the sliced granules resulting from the treatment of 2D ZnGA with $\text{H}_3\text{Co}(\text{CN})_6$. The diffraction peaks of $\text{H}_3\text{Co}(\text{CN})_6$ were not detected in the PXRD pattern of Co-ZnGA. In addition, the diffraction peaks of classical double metal cyanide catalysts, $\text{Zn}_3(\text{Co}(\text{CN})_6)_2 \cdot \text{H}_2\text{O}$ (2θ at 14.9 , 17.4 , 24.5 , 34.9 , 39.2 , and 43.1°) were not observed in Co-ZnGA.²³

The IR spectrum of 2D ZnGA showed glutarate moiety vibration peaks at 1537 (COO^-), 1447 (CH_2), and 1405 cm^{-1} (COO^-), which is consistent with that of conventional ZnGA reported in the literature (Fig. 4b).²⁴ The Co-ZnGA IR spectrum displayed a CN vibration peak at 2188 cm^{-1} , in addition to those of ZnGA, indicating that the cobalt cyanide moieties were successfully incorporated into the Co-ZnGA. The solid-

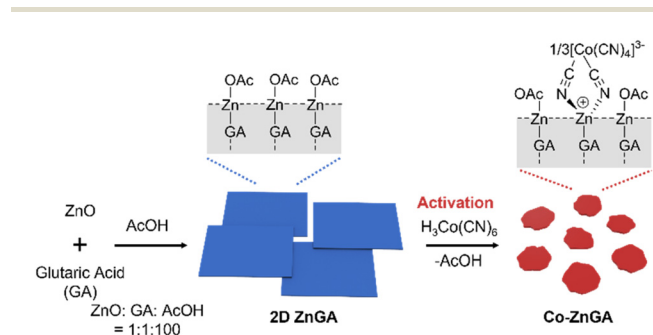


Fig. 2 Synthesis of ZnGA plates (2D ZnGA) and Co-modified 2D ZnGA (Co-ZnGA).

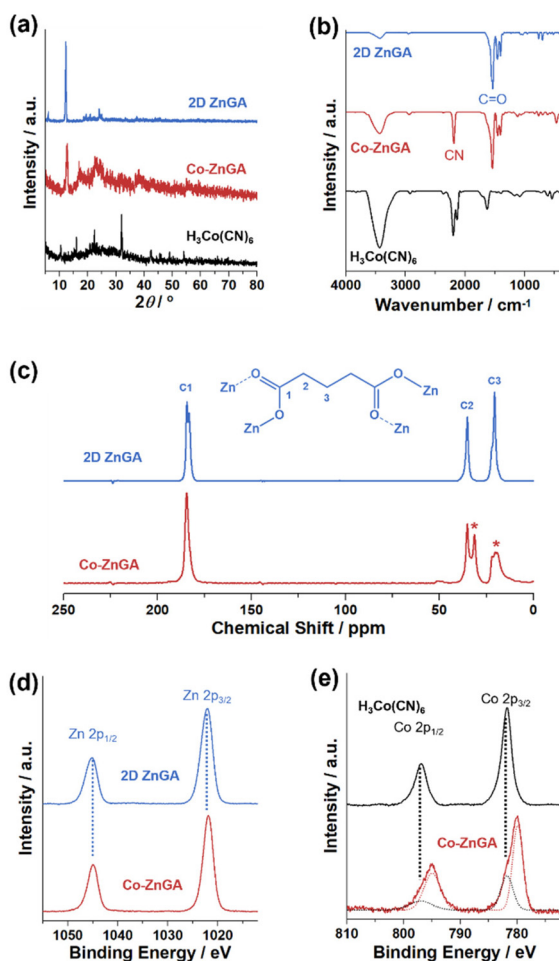


Fig. 4 (a) PXRD patterns, (b) IR spectra, (c) solid-state CP-TOSS ^{13}C NMR spectra (peaks labelled with * at 31 and 19 ppm correspond to glutarate moieties near active zinc sites), (d) XPS Zn 2p orbital spectra, and (e) XPS Co 2p orbital spectra of 2D ZnGA and Co-ZnGA, and $\text{H}_3\text{Co}(\text{CN})_6$.

state CP-TOSS ^{13}C NMR spectrum of 2D ZnGA showed three main ^{13}C peaks at 184, 35, and 21 ppm, respectively corresponding to the coordinated glutarate moieties (Fig. 4c). The peaks corresponding to the acetate moiety of 2D ZnGA are not distinguishable by the solid-state NMR.²⁵ The solution NMR of the reaction mixture of 2D ZnGA and aqueous HCl exhibited peaks at 2.18 and 1.61 ppm corresponding to glutarates and 1.81 ppm corresponding to acetates which were dissociated from 2D ZnGA upon the acid treatment (see ESI, Fig. S4†). Co-ZnGA showed two additional ^{13}C peaks at 31 and 19 ppm, corresponding to glutarate moieties near active zinc sites resulting from the ligand exchange reaction.

The chemical environment of metals in 2D ZnGA and Co-ZnGA was investigated using X-ray photoelectron spectroscopy (XPS) (Fig. 4d and e). While the XPS $2p_{1/2}$ and $2p_{3/2}$ orbital peaks of Zn species in 2D ZnGA were observed at 1045.2 and 1022.0 eV, respectively, those of Zn species in Co-ZnGA appeared at 1045.0 and 1021.9 eV, respectively (Fig. 4d). Because the primary Zn species in 2D ZnGA and Co-ZnGA is

ZnGA, the XPS 2p orbital peaks of Zn species in 2D ZnGA and Co-ZnGA were not significantly different (Fig. 4d). In comparison, while the XPS $2p_{1/2}$ and $2p_{3/2}$ orbital peaks of Co species in $\text{H}_3\text{Co}(\text{CN})_6$ appeared at 797.0 and 781.8 eV, respectively, those of Co species in Co-ZnGA shifted substantially to 795.0 and 779.9 eV, respectively (Fig. 4e), indicating the reaction of $\text{H}_3\text{Co}(\text{CN})_6$ in the conversion of 2D ZnGA into Co-ZnGA. Based on the deconvoluted XPS spectra of Co-ZnGA, small amounts of $\text{H}_3\text{Co}(\text{CN})_6$ or another cobalt species might exist in Co-ZnGA. Moreover, the XPS spectra of Zn $2p_{3/2}$ (1021.9 eV) and Co $2p_{3/2}$ orbital (779.9 eV) of Co-ZnGA were different from the DMC catalyst with a chemical formula of $\text{Zn}_3(\text{Co}(\text{CN})_6)_2$; Zn $2p_{3/2}$ (1022.5 eV) and Co $2p_{3/2}$ orbital peaks (780.7 and 782.6 eV) were observed in the XPS spectra of $\text{Zn}_3(\text{Co}(\text{CN})_6)_2$ (see ESI, Fig. S5†).²⁶

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to analyse the amount of Zn in the 2D ZnGA and was found to comprise 34.8 wt%, corresponding to 5.32 mmol g^{-1} . Those of Zn and Co in Co-ZnGA were analysed to be 31.5 and 6.31 wt%, corresponding to 4.82 and 1.07 mmol g^{-1} , respectively. The ratio of Zn : Co on the surface of the catalyst was evaluated by transmission electron microscopy (TEM) equipped with energy-dispersive spectroscopy (EDS), showing 2 : 1 ratio of Zn : Co (see ESI, Fig. S6†). The ratio of Zn and Co of the bulk Co-ZnGA (Zn : Co = 4.5 : 1) is higher than that of the surface (Zn : Co = 2 : 1), indicating higher concentration of Co species at the surface. Thermogravimetric analysis (TGA) was performed and the Co-ZnGA was observed to be thermally stable up to 315 °C (see ESI, Fig. S7†).

The polymerization of CO_2 and propylene oxide (PO) was optimized as listed in Table 1. Besides the polycarbonate-polyether product, cyclic carbonates were observed as a side product. Catalyst 1 (Co-ZnGA 1) was prepared from conventional ZnGA and $\text{H}_3\text{Co}(\text{CN})_6$ at a ratio of 3 : 1 and subjected to the polymerization conditions using CO_2 and PO; and low catalytic activity was exhibited (entry 1 of Table 1). The conventional ZnGA-catalyzed polymerization displayed similar catalytic activity (33.1 g $\text{g}^{-1}\text{cat}^{-1}$) to that of Co-ZnGA 1 (24.4 g $\text{g}^{-1}\text{cat}^{-1}$) but higher incorporation of CO_2 (entries 1 and 2 of Table 1), demonstrating the detrimental effect of $\text{H}_3\text{Co}(\text{CN})_6$ on the surface of ZnGA. Instead of the conventional ZnGA, a morphology-controlled 2D ZnGA was used to form Co-ZnGA 2, which exhibited 397 g $\text{g}^{-1}\text{cat}^{-1}$ activity (entry 3 of Table 1). It was observed that 2D ZnGA did not form polymers, due to the reduced number of defects (entry 4 of Table 1).^{19,27} The ratios of 2D ZnGA and $\text{H}_3\text{Co}(\text{CN})_6$ were adjusted to ratios of 3 : 1, 2 : 1, and 4 : 1, respectively during the synthesis of Co-ZnGA catalysts 2, 3, and 4 (entries 3, 5, and 6, respectively), with Co-ZnGA 2 (ratio of 3 : 1 of 2D ZnGA to $\text{H}_3\text{Co}(\text{CN})_6$) displaying the highest catalytic activity. The surface area of catalysts 2, 3, and 4 is 215, 119, and 88 $\text{m}^2 \text{g}^{-1}$, respectively, and the porosity of catalysts 2, 3, and 4, is 0.28, 0.24, and 0.20 $\text{cm}^3 \text{g}^{-1}$, respectively (Fig. 3(c) and see ESI, Fig. S2†). The high catalytic activity might be related to the high surface area and porosity, but the catalytic activity did not proportionally increase upon increasing the surface area based on the results of Co-ZnGA 3 and 4.

Table 1 Co-ZnGA-catalyzed polymerization of propylene oxide and CO₂

$\text{CO}_2 + \text{PO} \xrightarrow[\text{20 h}]{\text{catalyst, temp}} \left[\text{O}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}(\text{Me})-\text{O} \right]_x \left[\text{O}-\text{CH}_2-\text{CH}_2-\text{O} \right]_y + \text{cyclic carbonate}$									
Entry	Catalyst (mg g-PO ⁻¹)	CO ₂ (bar)	Temp.	Yield (g g-cat ⁻¹)	<i>f</i> _{CO₂}	Selectivity	<i>M</i> _n (kDa)	<i>D</i>	<i>T</i> _g (°C)
1	Co-ZnGA 1 (2.0)	40	80 °C	24.4	0.24	83%	—	—	—
2	ZnGA (11)	40	80 °C	33.1	0.95	72%	49.3	1.8	33
3	Co-ZnGA 2 (2.0)	40	80 °C	397	0.57	86%	42.3	2.1	16
4	2D ZnGA (11)	40	80 °C	—	—	—	—	—	—
5	Co-ZnGA 3 (2.0)	40	80 °C	194	0.51	87%	30.1	3.4	23
6	Co-ZnGA 4 (2.0)	40	80 °C	305	0.58	82%	51.7	1.9	22
7	Co-ZnGA 5 (2.0)	40	80 °C	39.3	0.44	78%	50.0	3.1	12
8	Co-ZnAc (2.0)	40	80 °C	8.5	0.63	90%	5.5	8.0	—
9	Co-ZnGA 2 (1.0)	40	80 °C	621	0.60	86%	48.6	2.1	18
10	Co-ZnGA 2 (1.0)	30	80 °C	521	0.56	84%	59.6	2.6	20
11	Co-ZnGA 2 (1.0)	40	90 °C	855	0.61	82%	72.6	1.9	20
12	Co-ZnGA 2 (1.0)	40	100 °C	368	0.59	79%	39.6	2.9	23
13	Classical DMC ²⁸	40	90 °C	1093	0.26	92%	87.8	2.9	10

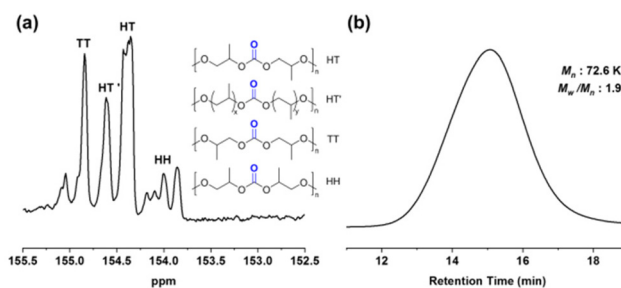
Polymerization conditions: PO (4.36 g, 75 mmol) was used. *f*_{CO₂}: {[PPC]}/([PPC] + [PPO]) determined by ¹H NMR, selectivity: [PO incorporated into polymer]/([propylene carbonate] + [PO incorporated into polymer]) determined by ¹H NMR, *M*_n, *M*_w/*M*_n: determined by GPC using a polystyrene standard. Co-ZnGA 1: H₃Co(CN)₆ with conventional ZnGA (3 equiv.); Co-ZnGA 2: H₃Co(CN)₆ with 2D ZnGA (3 equiv.); Co-ZnGA 3: H₃Co(CN)₆ with 2D ZnGA (2 equiv.); Co-ZnGA 4: H₃Co(CN)₆ with 2D ZnGA (4 equiv.); Co-ZnGA 5: H₃Co(CN)₆ with Zn(OAc)₂ (3 equiv.) and glutaric acid (3 equiv.); Co-ZnAc: H₃Co(CN)₆ with Zn(OAc)₂ (3 equiv.).

The preparation of Co-ZnGA 5 involved combining H₃Co(CN)₆, Zn(OAc)₂, and glutaric acid, and the results exhibited a low yield (39.3 g g-cat⁻¹) (entry 7 of Table 1). By comparing the results from Co-ZnGA 2 and Co-ZnGA 5, it is evident that the morphology of 2D ZnGA and composition of Co-ZnGA are crucial for polymerization. Polymers with low activity were formed by Co-ZnAc derived from H₃Co(CN)₆ and Zn(OAc)₂ (entry 8 of Table 1). The reduced catalyst loadings (1 mg g-PO⁻¹) of Co-ZnGA 2 were examined, and an increased catalytic activity of 621 g g-cat⁻¹ was observed (entry 9). The pressure and temperature were varied, resulting in lower catalytic activity (521 g g-cat⁻¹) at the lower pressure of CO₂ (30 bar) and the highest catalytic activity (855 g g-cat⁻¹) at 90 °C (entries 10–12). The catalytic activity of the classical double metal cyanide,²⁸ Zn₃[Co(CN)₆]₂ was measured, showing higher catalytic activity but much lower *f*_{CO₂} value (1093 g g-cat⁻¹ and *f*_{CO₂} = 0.26) (entry 13).

The *f*_{CO₂} and selectivity of polymers were calculated based on ¹H NMR spectra (see ESI, Fig. S8–S21†). Catalysts derived from 2D ZnGA and H₃Co(CN)₆ formed polymers with *f*_{CO₂} values of 0.51–0.61. The catalyst composition (the ratio of Zn and Co), the reaction temperature, and the CO₂ pressure were varied, exhibiting similar CO₂ contents. According to Reiger's report,¹⁹ the elongated zinc–zinc distance can induce PO homopolymerization, lowering the carbonate linkages' fraction. Accordingly, the elongated zinc–zinc distance in Co-ZnGA 2 can be speculated, resulting in the observed *f*_{CO₂} values. The CO₂ contents in the polymers composed of polycarbonate and polyether units affect *T*_g and thermal stability, which expands the utility of this polymer.^{29,30} Polymers formed by Co-ZnGA 2 (entry 11 of Table 1) exhibited *T*_g = 20 °C (*f*_{CO₂} = 0.61) (see ESI, Fig. S22†), which is lower than that of polypropylene carbonate

(*T*_g = 38 °C) and higher than that of polypropylene glycol (*T*_g = –68 °C).²⁹ The thermal stability of the polymer was estimated by TGA analysis. The onset decomposition temperature of the polymer sample (entry 11 of Table 1) was 254 °C (see ESI, Fig. S24†), which is comparable to that of polypropylene carbonate (251 °C).²

The structure of polymers (entry 11 of Table 1) was analysed by ¹³C NMR spectrum, showing carbonyl peaks at 154.9, 154.6, 154.4, and 154.0 ppm (Fig. 5a). The previous report assigned carbonyl peaks of alternating polycarbonates at 154.8 ppm as TT, 154.3 ppm as HT, and 154.0 ppm as HH.³¹ In the case of polycarbonate-ether, another peak corresponding to HT' at 154.5 ppm was observed, along with the increased ratio of the TT peak.³² The HT' peak at 154.5 ppm is the carbonyl peak, involving more than two PO units connected to the carbonyl group.³¹ Compared with the previous analysis, the polymer obtained in this work is composed of alternating and non-alternating polycarbonates, where HT and HT' carbonyl peaks

**Fig. 5** (a) ¹³C NMR spectrum of the C=O region and (b) GPC of entry 11 (Table 1).

at 154.4 and 154.6 are major, respectively. The polymers formed from Co-ZnGA 2-catalyzed reactions at 80 °C show a molecular weight of approximately 50 000. The highest molecular weight ($M_n = 72\,600$) was observed at 90 °C (Fig. 5b), and further increasing the temperature to 100 °C caused lower activity and molecular weight.

Substituted epoxides underwent polymerization with CO₂ in the presence of Co-ZnGA 2, which formed thermoplastic polymers that can be utilized for coating and packing materials, ceramic binders, adhesives, and biomedical applications.^{33,34} The substituent on the epoxide may affect the catalytic activity and selectivity of the steric hindrance during polymerization. The reactions of 1,2-epoxyhexane with CO₂ showed high catalytic activity, CO₂ fraction, and selectivity (1540 g g-cat⁻¹, $f_{\text{CO}_2} = 0.91$, selectivity = 74%). The reactions of 1,2-epoxybutane with CO₂ formed polymers with catalytic activity, CO₂ fraction, and selectivity of 1190 g g-cat⁻¹, $f_{\text{CO}_2} = 0.83$, and 68%, respectively. Compared to the reactions of epoxides substituted with aliphatic groups (methyl, ethyl, and butyl), styrene oxide reacted with CO₂, forming polymers with low catalytic activity (148 g g-cat⁻¹); however, CO₂ fraction and selectivity were higher than those of the aliphatic group substituted epoxides. The f_{CO_2} and selectivity of entries 1–3 (Table 2) were calculated based on ¹H NMR spectra (see ESI, Fig. S19–S21†). In these polymerization reactions, cyclic carbonates were observed as a side product. Overall, the sterically bulky group on the epoxide increases the CO₂ fraction and selectivity. The electronic properties of the substituent may affect catalytic activity. The dispersity ($\bar{D}$), T_g , and onset decomposition temperature of polymers were 1.5–4.7, –8.7–48 °C, and 281–289 °C, respectively (see ESI, Fig. S23, S25–S27, and S37–S39†).

After optimizing the polymerization, the mechanical properties of the polymer samples were investigated under tensile strain (Fig. 6, and see ESI, Videos S1 and S2†). Two polymer samples, one with a methyl side chain and the other with an ethyl side chain were fabricated into the rectangular test bar using the hot press technique. The tensile tests of the polymer

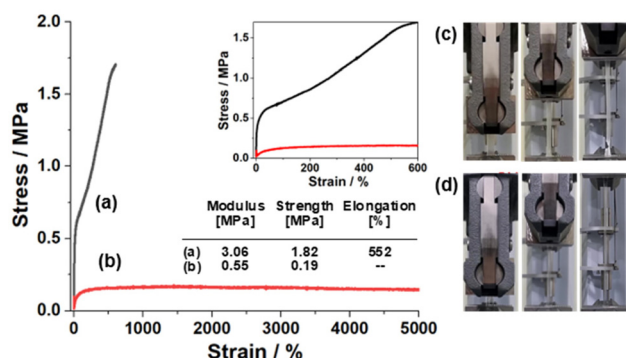


Fig. 6 Tensile strength of polymers of (a) entry 11 in Table 1 and (b) entry 2 in Table 2, inset: the enlarged graph showing tensile strength of (a) and (b) ranging from a strain of 1 to 600%. Photographs of tensile strength tests of polymers of entry 11 in Table 1 (c) and entry 2 in Table 2 (d).

samples involving the butyl group in entry 1 (Table 2) and the phenyl group in entry 3 (Table 2) were not performed due to the poor quality of the test bar obtained. The polymer involving the methyl group and 61% carbonate linkage, exhibited elastomeric behaviour with moderate elongation and stress break values of 552% and 1.82 MPa, respectively (Fig. 6a and Table 1, entry 11). The ultimate strength value of the polymer involving the ethyl group and 83% of carbonate linkage was reduced to 0.19 MPa, and the breakage of this sample was not detected in the tested strain range up to 5000% (Fig. 6b and Table 2, entry 2). The polymer containing the methyl group exhibited relatively higher values of tensile strength and Young's modulus, which might be attributed to the higher T_g value than that of the ethyl group (20 vs. 7 °C).

The advantageous catalytic activity of Co-ZnGA catalysts is demonstrated by the mechanism presented in Fig. 7. The Co-ZnGA catalysts involve both $[\text{ZnGA}]^+[\text{Co}]^-$ ($[\text{Co}]^- = 1/3[\text{Co}(\text{CN})_6]^{3-}$) and $\text{ZnGA}(\text{OAc})$ at the reaction sites. The ratio

Table 2 Co-ZnGA 2-catalyzed copolymerization of epoxides with CO₂

$\text{CO}_2 + \text{Epoxide-R} \xrightarrow[20\text{ h}]{\text{Co-ZnGA 2, } 90^\circ\text{C}} \left[\text{O}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}(\text{R})-\text{O} \right]_x \left[\text{O}-\text{CH}_2-\text{CH}_2-\text{O} \right]_y + \text{Cyclic carbonate-R}$							
Entry	R	Yield (g g-cat ⁻¹)	f_{CO_2}	Selectivity	M_n (kDa)	$\bar{D}$	T_g (°C)
1	C ₄ H ₉	1540	0.91	74%	50.0	3.1	–8.7
2	C ₂ H ₅	1190	0.83	68%	36.5	4.7	7.1
3	C ₆ H ₅	148	>0.99	88%	8.2	1.5	48

Polymerization conditions: Co-ZnGA 2 (4.4 mg), epoxide (75 mmol), and CO₂ (40 bar) was used. f_{CO_2} : $\{[\text{polycarbonate}]\}/\{[\text{polycarbonate}] + [\text{polyether}]\}$ determined by ¹H NMR, selectivity: $[\text{epoxide incorporated into polymer}]/\{[\text{monomer carbonate}] + [\text{epoxide incorporated into polymer}]\}$ determined by ¹H NMR, M_n , M_w/M_n : determined by GPC using a polystyrene standard.

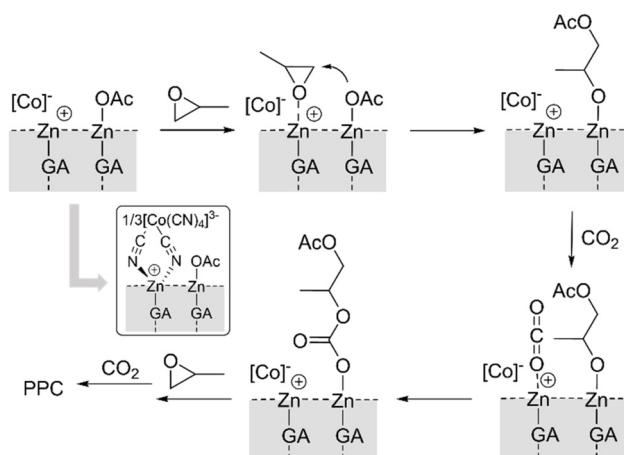


Fig. 7 Proposed mechanism of the Co-ZnGA-catalyzed polymerization of CO₂ and propylene oxide. The coordination of cyanides of $[\text{Co}]^-$ was omitted for the clear demonstration.

of Zn:Co was 4.5:1 (by ICP-AES analysis) and 2:1 (by TEM-EDS), indicating that a portion of ZnGA(OAc) species are converted to $[\text{ZnGA}]^+[\text{Co}]^-$. $[\text{ZnGA}]^+[\text{Co}]^-$ and ZnGA(OAc) interact cooperatively to induce polymerization. Epoxides may coordinate to the active reaction site $[\text{ZnGA}]^+[\text{Co}]^-$, where the zinc ion is coordinated by cyanides.³⁵ Then, Zn-alkoxides are formed by the subsequent ring opening of epoxides by acetate.³⁶ The Zn–O bonds form Zn-carbonate intermediates when CO_2 is inserted. A chain propagation, in proximity to the Zn-carbonates takes place with the coordination of epoxides to $[\text{ZnGA}]^+[\text{Co}]^-$ and is followed by the carbonate addition to epoxides.²¹ As proposed in homogeneous Zn-catalyzed polymerization of epoxides and CO_2 ,³⁷ the optimal concentration of $[\text{ZnGA}]^+[\text{Co}]^-$ at the surface of Co-ZnGA is crucial for the high catalytic activity in polycarbonate synthesis.³⁸

3. Conclusions

We present a new method for forming morphology-controlled ZnGA (2D ZnGA) and associated activation for the efficient polymerization of CO_2 and epoxides. The treatment of 2D ZnGA with $\text{H}_3\text{Co}(\text{CN})_6$ formed activated Co-ZnGA that exhibited highly improved catalytic activity in the copolymerization of various epoxides and CO_2 , while the conventional ZnGA showed low catalytic activity. Substantially increased catalytic activity was demonstrated by the surface activation and increased surface area and porosity of Co-ZnGA catalysts. The Co-ZnGA catalysts derived from 2D ZnGA with $\text{H}_3\text{Co}(\text{CN})_6$ at a ratio of 3:1 resulted in the highest activity polymerization 855 g g-cat⁻¹ with PO, 1540 g g-cat⁻¹ with 1,2-epoxyhexane, 1190 g g-cat⁻¹ with 1,2-epoxybutane, and 148 g g-cat⁻¹ with styrene oxide. The physical properties of polymers were evaluated, and correlation between T_g and tensile strength was observed.

4. Experimental

4.1 General

Anhydrous solvents were transferred by an oven dried syringe. Solvents were distilled prior to use. Propylene oxide was dried by stirring over CaH_2 and then vacuum-transferred to a reservoir. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded with a Jeol Resonance ECZ600R (600 MHz) spectrometer. Number average molecular weights (M_n) and weight average molecular weights (M_w) were calculated relative to linear polystyrene standards. Dispersity (D) values are reported as the quotient of M_w/M_n . Differential scanning calorimetry (DSC) was carried out under N_2 gas at a scan rate of 10 °C min⁻¹ with DSC 200 F3 Maia from NETZSCH. SEM images were obtained using a JSM6700. N_2 adsorption-desorption isotherm curves were obtained using a Micromeritics ASAP2460. The surface areas and porosity of materials were characterized based on the Brunauer-Emmett-Teller (BET) theory. Pore size distribution diagrams were obtained by the

DFT method. IR spectra were obtained using a Bruker VERTEX 70 FT-IR spectrometer. XPS spectra were obtained using a Thermo VG spectrometer. Solid state ¹³C nuclear magnetic resonance (NMR) spectra were obtained at a cross-polarization/total side band suppression (CP/TOSS) mode using a 500 MHz Bruker ADVANCE II NMR spectrometer at the National Center for Inter-University Research Facilities (NCIRF) of Seoul National University. PXRD patterns were obtained using a Rigaku MAX-2200. TGA curves were obtained using a Seiko Exstar 7300. ICP-AES analysis was conducted using an OPTIMA8300.

4.2 Experimental procedure for the synthesis of catalysts

2D ZnGA. For the preparation of 2D ZnGA, zinc oxide (250 mg, 3.07 mmol) was suspended in acetic acid (17.6 mL) through vigorous stirring (1150 rpm) in a flame-dried 100 mL Schlenk flask. After glutaric acid (406 mg, 3.07 mmol), and distilled toluene (18 mL) were added, the reaction mixture was stirred at 50 °C for 24 h. After the reaction mixture was cooled to room temperature, the solid (2D ZnGA) was separated by centrifugation, washed with acetone (40 mL) five times, and dried under vacuum at 80 °C for overnight.

Co-ZnGA 2. For the preparation of Co-ZnGA 2, 2D ZnGA (213 mg, 1.08 mmol) was suspended in distilled methanol (3.8 mL) in a vacuum dried 5 mL round-bottom flask through sonication for 1 h. After $\text{H}_3\text{Co}(\text{CN})_6$ (121 mg, 0.360 mmol) in distilled methanol (2.5 mL) was added quickly, the reaction mixture was stirred vigorously at room temperature for 24 h. The white solid (Co-ZnGA 2) was separated by centrifugation, washed with anhydrous methanol (1.0 mL) three times, and dried under vacuum at room temperature for 5 days (150 mg).

Co-ZnGA 5. For the preparation of Co-ZnGA 5, Zn(OAc)₂ (198 mg, 1.08 mmol) and glutaric acid (143 mg, 1.08 mmol) were suspended in distilled methanol (3.8 mL) in a vacuum dried 25 mL round-bottom flask through sonication for 1 h. Then, $\text{H}_3\text{Co}(\text{CN})_6$ (121 mg, 0.360 mmol) in distilled methanol (2.5 mL) was added quickly to the reaction mixture. The resulting mixture was stirred vigorously at room temperature for 24 h. The white solid (Co-ZnGA 5) was separated by centrifugation, washed with anhydrous methanol (1.0 mL) three times, and dried under vacuum at room temperature (130 mg).

4.3 Polymerization procedure

Copolymerization of propylene oxide and CO_2 . An autoclave (50 mL) was assembled after charging with a magnetic stirring bar, Co-ZnGA 2 (8.7 mg) and propylene oxide (PO) (4.36 g, 75 mmol). The autoclave was pressurized with CO_2 gas to 40 bar at room temperature. And then immersed in an oil bath at room temperature. The reaction mixture was stirred (250 rpm) and heated at 80 °C for 20 hours. After being cooled to room temperature and vented unreacted CO_2 gas, the polymerization solution was transferred to 100 mL round-bottom flask by dissolving with dichloromethane, and all volatiles were removed using a rotary evaporator, leaving a waxy solid. The solid was recrystallized in dichloromethane and methanol mixture.

Copolymerization of 1-hexene oxide and CO₂. An autoclave (50 mL) was assembled after charging with a magnetic stirring bar, Co-ZnGA 2 (4.4 mg) and 1-hexene oxide (HO) (7.51 g, 75 mmol). The autoclave was pressurized with CO₂ gas to 40 bar at room temperature. And then immersed in an oil bath at room temperature. The reaction mixture was stirred (250 rpm) and heated at 90 °C for 20 hours. After being cooled to room temperature and vented unreacted CO₂ gas, and the polymerization solution was transferred to 100 mL round-bottom flask by dissolving with dichloromethane, and all volatiles were removed using a rotary evaporator, leaving a waxy solid. The solid was recrystallized in dichloromethane and methanol mixture.

Copolymerization of 1,2-butylene oxide and CO₂. An autoclave (50 mL) was assembled after charging with a magnetic stirring bar, Co-ZnGA 2 (4.4 mg) and 1,2-butylene oxide (BO) (5.41 g, 75 mmol). The autoclave was pressurized with CO₂ gas to 40 bar at room temperature. And then immersed in an oil bath at room temperature. The reaction mixture was stirred (250 rpm) and heated at 90 °C for 20 hours. After being cooled to room temperature and vented unreacted CO₂ gas, and the polymerization solution was transferred to 100 mL round-bottom flask by dissolving with dichloromethane, and all volatiles were removed using a rotary evaporator, leaving a waxy solid. The solid was recrystallized in dichloromethane and methanol mixture.

Copolymerization of styrene oxide and CO₂. An autoclave (50 mL) was assembled after charging with a magnetic stirring bar, Co-ZnGA 2 (4.4 mg) and styrene oxide (SO) (9.01 g, 75 mmol). The autoclave was pressurized with CO₂ gas to 40 bar at room temperature. And then immersed in an oil bath at room temperature. The reaction mixture was stirred (250 rpm) and heated at 90 °C for 20 hours. After being cooled to room temperature and vented unreacted CO₂ gas, and the polymerization solution was transferred to 100 mL round-bottom flask by dissolving with dichloromethane, and all volatiles were removed using a rotary evaporator, leaving a solid. The solid was recrystallized in dichloromethane and methanol mixture.

Author contributions

S. U. Son, H.-Y. Jang: conceptualization, supervision, writing original draft, and review & editing. Y. Yang, J. D. Lee: investigation and formal analysis. Y. H. Seo, J.-H. Chae, S. Bang, Y.-J. Cheong, B. Y. Lee, I.-H. Lee: methodology.

Conflicts of interest

There are no conflicts to declare.

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