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## Pressure-dependent CO<sub>2</sub> thermolysis on barium titanate nanocatalysts†

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Rising CO<sub>2</sub> levels pose a significant threat to global warming, extreme weather events, and ecosystem disruption. Mitigating these effects requires a reduction in CO<sub>2</sub> concentration using innovative technologies for CO<sub>2</sub> capture, storage, and utilization. Perovskite-type barium titanate nanocatalysts have the potential for high CO<sub>2</sub> conversion into valuable solid carbon products at low temperatures. In this study, we investigated the pressure-dependent CO<sub>2</sub> conversion activity of barium titanate nanocatalysts at 700 K. A key focus of this study is the impact of pressure on the interaction between CO<sub>2</sub> molecules and barium titanate nanocatalysts to evaluate the CO<sub>2</sub> conversion mechanism. The primary structures of the nanocatalysts remained unchanged after CO<sub>2</sub> thermolysis, whereas carbon was deposited on the nanocatalysts above 0.05 MPa. The reactant carbons after CO<sub>2</sub> conversion at various pressures between 0.01 and 1.0 MPa at 700 K were evaluated by temperature-programmed desorption in an O<sub>2</sub> atmosphere. The desorption peaks observed at approximately 500 K, 800–900 K, and 900–1300 K were the results of desorption of chemisorbed CO<sub>2</sub>, less- and high-crystalline graphitic carbons. Chemisorbed CO<sub>2</sub> and less-crystalline graphitic carbon were observed at 0.05 MPa. Highly crystalline graphitic carbons were observed on the nanocatalysts after CO<sub>2</sub> thermolysis at 0.1–1.0 MPa as well as chemisorbed CO<sub>2</sub>, although the amount of carbon at 1.0 MPa was smaller than the others. Therefore, the approach of CO<sub>2</sub> thermolysis at a low temperature of 700 K and 0.1–0.5 MPa is promising for producing valuable solid carbon products and mitigating the environmental impact of CO<sub>2</sub> emissions.

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### Sustainability spotlight

Rising CO<sub>2</sub> levels significantly influence global warming, extreme weather events, and disruptions to ecosystems. Mitigating these effects requires innovative CO<sub>2</sub> capture, storage, and utilization technologies. Nanocatalysts have the potential for high CO<sub>2</sub> conversion into valuable solid carbon products at low temperatures. In this study, we investigated the pressure-dependent CO<sub>2</sub> conversion activity of perovskite-type BaTiO<sub>3</sub> nanocatalysts at 700 K. In particular, we investigate the impact of pressure on the interaction between CO<sub>2</sub> molecules and BaTiO<sub>3</sub> nanocatalysts and evaluate the key reaction mechanism and pressure dependence of CO<sub>2</sub> thermolysis. This study is essential for optimizing reaction conditions and maximizing CO<sub>2</sub> conversion efficiency using more sustainable technology.

## Introduction

CO<sub>2</sub> is a prominent element in the progression of climate alterations, such as extreme weather phenomena encompassing wildfires, droughts, hurricanes, heatwaves, and rising sea levels due to a rise in worldwide temperature.<sup>1</sup> CO<sub>2</sub> concentration in the atmosphere rose to 417.2 ppm in 2022, with a 2.5 ppm increase every year, despite the concentration of approximately 280 ppm during the 1800 s.<sup>2</sup> This upward trend has been a concern for humanity. The surge in CO<sub>2</sub> concentration is primarily attributable to heightened energy consumption, deforestation, and combustion of fossil fuels. The objective of

the Paris Agreement is to limit the global average temperature rise to significantly less than 2 °C compared with that in the preindustrial era. To realize this goal, CO<sub>2</sub> emissions must be cut by 50% by 2030, and a net-zero status should be achieved by 2050.<sup>3</sup> Carbon capture, utilization, and storage technology is the key to combating global warming, in which CO<sub>2</sub> emissions are mitigated by capturing and storing CO<sub>2</sub> and converting it into highly valuable products.<sup>4</sup>

Adsorption is the most mature technology for capturing CO<sub>2</sub>. Various novel nanomaterials have been employed to capture CO<sub>2</sub> from flue gas using zeolites, metal–organic frameworks (MOFs), carbon materials, mesoporous silica, and metal oxides. These materials possess high specific surface areas, exceptional selectivity, superior thermal and chemical stability, and various other advantageous properties. For instance, the CO<sub>2</sub> adsorption capacities of zeolites ZSM-5, LEZ-Zeolite Na(X), and Na(Y) are 5.2, 0.7, 5.14, and 7.06 mmol g<sup>-1</sup>, respectively, at room

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temperature and ambient pressure.<sup>5,6</sup> MOFs MOF-177, MIL-100(Fe), and MIL-101(Cr) exhibit CO<sub>2</sub> adsorption capacities of 33.5, 0.67, and 1.05 mmol g<sup>-1</sup>, respectively.<sup>7,8</sup> Chen and co-workers reported CO<sub>2</sub> adsorption capacities of 2.7–5 and 0.2–3 mmol g<sup>-1</sup> on activated carbons and carbon nanotubes (CNTs) at 273 K below 0.1 MPa.<sup>9</sup> Zafanelli and co-workers reported activated carbons adsorbed up to 3.17 mmol g<sup>-1</sup> CO<sub>2</sub> at 586 K and 0.12 MPa.<sup>10</sup> Osler and co-workers reported that multiwalled CNT/chitosan composite had an adsorption capacity of 0.07 mmol g<sup>-1</sup>.<sup>11</sup> Amine-based adsorbents exhibit an adsorption capacity of 0.03 mmol g<sup>-1</sup> at 348 K and ambient pressure.<sup>12</sup> Metal oxides, such as Ce and Mn–CaO, demonstrate high CO<sub>2</sub> adsorption capacities, reaching 14 mmol g<sup>-1</sup> at a high temperature of 1046 K and 0.1 MPa.<sup>13</sup>

Converting CO<sub>2</sub> through chemical processes is a challenging endeavor, because of the remarkable thermodynamic stability of CO<sub>2</sub> molecules.<sup>14</sup> The breaking of the chemical bonds in CO<sub>2</sub> requires substantial energy. Researchers have devised innovative approaches to overcome this challenge using catalysts. An example involves the use of nanomaterial-based catalysts, along with operating under high pressure and temperature conditions.<sup>15</sup> Although these techniques effectively satisfy the energy demands for CO<sub>2</sub> conversion, rendering the process more attainable, high temperature and pressure reactions can be energetically costly. Therefore, approaches for catalytic CO<sub>2</sub> conversion that are less energetic are required. Electrocatalytic, photocatalytic, and thermocatalytic methods are crucial techniques for converting CO<sub>2</sub> into valuable chemicals and fuels. In addition, CO<sub>2</sub> can be harnessed for mineral carbonation by leveraging metals such as calcium or magnesium to form carbonates.<sup>16</sup> Moreover, microalgal cultivation is a promising method for capturing CO<sub>2</sub> from waste streams and converting it into biofuels. However, it requires huge land areas, and process control is complex.<sup>17</sup> Photocatalytic CO<sub>2</sub> reduction exhibits remarkable selectivity, enabling the conversion of CO<sub>2</sub> into various carbon products, such as carbon monoxide (2003 μmol g<sup>-1</sup> h<sup>-1</sup>), formic acid (46 μmol g<sup>-1</sup> h<sup>-1</sup>), formaldehyde (1 μmol g<sup>-1</sup> h<sup>-1</sup>), methanol (186 μmol g<sup>-1</sup> h<sup>-1</sup>), methane (4200 μmol g<sup>-1</sup> h<sup>-1</sup>), acetic acid (39 μmol g<sup>-1</sup> h<sup>-1</sup>), acetaldehyde (572 μmol g<sup>-1</sup> h<sup>-1</sup>), and ethanol (52 μmol g<sup>-1</sup> h<sup>-1</sup>), using ruthenium-based catalysts, gold nanoparticles supported on TiO<sub>2</sub> sheets, carbon nitride–CdS quantum dots, alumina silicates, and titanium-based catalysts.<sup>18–25</sup>

Thermocatalytic CO<sub>2</sub> conversion is another potential method for achieving efficient CO<sub>2</sub> conversion. Thermocatalytic methanation involves the conversion of CO<sub>2</sub> into methane using a Ca-inserted NiTiO<sub>3</sub> perovskite catalyst with H<sub>2</sub> as a reduction gas at 623 K, achieving an impressive 87.32% conversion rate,<sup>26</sup> which is called the Sabatier reaction. In the chemical scheme, CO<sub>2</sub> and H<sub>2</sub> combine in the presence of a suitable catalyst, often a metal catalyst such as nickel, to yield methane and water, typically within the temperature range of 473–823 K.<sup>27</sup> The reverse water–gas shift reaction is predominant to generate CO from CO<sub>2</sub> and H<sub>2</sub> above 873 K. CO can serve as a precursor for a wide array of chemical applications, including its role in the Fischer–Tropsch synthesis to produce liquid fuels.<sup>28</sup> The hydrogenation of CO<sub>2</sub> can also result in the formation of

methanol when hydrogen gas is present along with a catalyst-based metal.<sup>29</sup> CO<sub>2</sub> is directly converted into solid carbon materials, including CNTs or graphene, by increasing the temperature and pressure. The direct conversion of CO<sub>2</sub> into solid carbon is the subject of ongoing research for carbon capture and utilization. Carbon materials are widely used in various applications, including energy storage, batteries, supercapacitors, drug delivery, water purification, electrodes, and catalyst support.<sup>30–32</sup> Diamond can be generated from CO<sub>2</sub> through the LiCl–Li<sub>2</sub>O molten salt method; CO<sub>2</sub> conversion into diamond involves subsequent conversion into Li<sub>2</sub>CO<sub>3</sub> crystals.<sup>33</sup> Graphite is synthesized at 1048 K using a CO<sub>2</sub> and SO<sub>2</sub> gas mixture in molten salts of Li<sub>2</sub>CO<sub>3</sub>–Na<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub>–Li<sub>2</sub>SO<sub>4</sub>.<sup>34</sup> The electrochemical method for carbon material production from CO<sub>2</sub> requires high operating temperatures exceeding 1023 K, because of the use of molten salts. Kim and co-workers produced CNTs at 773–873 K and 0.1 MPa using NaBH<sub>4</sub> and metallic Ni.<sup>35</sup> Despite this achievement, the development of CO<sub>2</sub> conversion technique at lower temperatures is required. We succeeded in converting CO<sub>2</sub> to graphitic carbon at 700 K and ambient pressure using perovskite-type titanium nanocatalysts with high reaction rates ranging from 1600 to 3300 μmol g<sup>-1</sup> h<sup>-1</sup>.<sup>36</sup> Nano-barium titanate is an effective adsorbent material, because of its substantial surface area and numerous active sites. In this study, we demonstrate pressure-dependent thermocatalytic CO<sub>2</sub> conversion to solid carbons from 0.01 to 1 MPa at 700 K using barium titanate nanocatalysts and evaluate the key mechanism with an elementary reaction process.

## Experimental

### Preparation of barium titanate nanocatalyst

Barium titanate nanocatalysts were synthesized using the solvothermal method in an N<sub>2</sub>-filled glove box. Each barium ethoxide and titanium tetraisopropoxide (>99%; Kojundo Chemical Laboratory Co., Saitama, Japan) were dissolved in a 10 mL methanol and methoxyethanol mixed solution, with a volume ratio of 3 : 2 (>99%; Fujifilm Wako Pure Chemical Co., Saitama, Japan) to prepare a 200 mM solution and then vigorously agitated for 3 h. Following the successful blending of the precursors, water was added to the precursor solution to maintain a molar ratio of Ba : Ti : H<sub>2</sub>O = 1 : 1 : 5. The mixture was heated in an autoclave at 400 K for 24 h. Finally, barium titanate nanocatalysts were obtained after drying at 333 K for one day in ambient air.

### Characterization of barium titanate nanocatalyst

The crystallinity of barium titanate nanocatalysts was evaluated by X-ray diffraction (XRD) (SmartLab, Rigaku Co., Tokyo, Japan) with Cu Kα radiation (wavelength λ = 0.1541 nm) at an X-ray generator voltage of 40 kV and current of 40 mA, within the 2θ range of 10–90°, employing an angular step size of 0.01°. The crystallite sizes of the nanocatalysts were determined using the Scherrer equation,<sup>37</sup> which relies on the full peak widths at half maximum. A Scherrer constant of 0.89 was used for calculations.



### Catalytic activity test

Barium titanate nanocatalysts were first heated at 700 K in an O<sub>2</sub> atmosphere for 24 h to eliminate surface contaminants before the catalytic activity test. The reaction stainless-steel cell with a quartz tube was also preheated at 700 K. A 200 mg barium titanate nanocatalyst was placed in a quartz tube supported by quartz wool. CO<sub>2</sub> adsorption and reactions on the nanocatalysts were initiated at 700 K after heating at a rate of 10 K min<sup>-1</sup>. CO<sub>2</sub> gas at 0.01, 0.05, 0.1, 0.5, and 1.0 MPa flowed in the reaction cell for 24 h. The catalyst weights before and after CO<sub>2</sub> adsorption/reaction were evaluated to determine the reaction amount of CO<sub>2</sub>. Thermogravimetric analysis (TGA; Thermo Plus EVO2, Rigaku Co., Tokyo, Japan) was also conducted to evaluate the amount of carbon reduced from CO<sub>2</sub> using the nanocatalysts after CO<sub>2</sub> adsorption/reaction. Reduced carbon was evaluated by Raman scattering spectroscopy with a Nd:YAG laser (532 nm) at a power of 0.1 mW (NRS-3000; JASCO Co., Tokyo, Japan) with an accumulation time of 300 s and 10–15 point average, TGA and transmission electron microscopy at 120 keV (TEM; JEM-2100F, JEOL Co., Tokyo, Japan). The D- and G-bands in the Raman spectra indicate the presence of amorphous and crystalline graphitic carbon in the barium titanate nanocatalysts, respectively. The weight changes of the nanocatalysts with reduced carbon were examined by TGA in an O<sub>2</sub> atmosphere (>99.7%) at a flow rate of 100 mL min<sup>-1</sup> at 300–1373 K. The rate of temperature increase was 10 K min<sup>-1</sup> and the air was replaced with Ar gas (>99.99%) at 300 K for 5 h before TGA measurements. We simultaneously employed carbon detection using a custom mass spectrometry system that includes BELL-MASS II (MicrotracBEL Co., Osaka, Japan) for temperature-programmed desorption (TPD) analyses in O<sub>2</sub> atmosphere. TPD measurements were performed using a TGA device. The evolved gases during the oxidation of nanocatalysts after CO<sub>2</sub> thermolysis are systematically analyzed in thermal reactions with O<sub>2</sub> gas (100 mL min<sup>-1</sup>) involving Ar gas (100 mL min<sup>-1</sup>) as a flowing gas in the temperature range of 300–1373 K. The exhaust gases were evaluated using mass spectrometry.

## Results and discussion

Barium titanate nanocatalysts have a high potential for CO<sub>2</sub> thermolysis, as reported elsewhere.<sup>36</sup> CO<sub>2</sub> was adsorbed/reduced onto the nanocatalyst surface, which influenced the nanocatalyst weights. CO<sub>2</sub> gas at 0.01–1.0 MPa was first introduced in a stainless cell with barium titanate nanocatalysts, and CO<sub>2</sub> thermolysis was performed on the nanocatalysts at 700 K. The amount of reduced carbon attached to the nanocatalysts was evaluated from the weight-decreasing curves of the nanocatalysts after CO<sub>2</sub> thermolysis in an O<sub>2</sub> atmosphere (Fig. S1†). That is, the weights of nanocatalyst with chemisorbed/reduced CO<sub>2</sub> were decreased by the removal of chemisorbed CO<sub>2</sub> and/or the oxidation of reduced carbon by heating in an O<sub>2</sub> atmosphere. The first decreasing step was a result of the removal of chemisorbed CO<sub>2</sub> at 300–600 K, and the reduced carbons were then oxidized above 600 K. The slight gradual increase in the amount at high temperatures above 1200 K was due to

additional oxidation of nanocatalyst itself in the O<sub>2</sub> atmosphere. Fig. 1a shows the amount of chemisorbed/reduced CO<sub>2</sub> at 0.01–1.0 MPa, as evaluated from the TGA in Fig. S1.† The CO<sub>2</sub> chemisorbed/reduced amounts considerably increased up to 670 μmol g<sup>-1</sup> in the low-pressure region between 0 and 0.05 MPa and gradually increased to 800 μmol g<sup>-1</sup> below 1 MPa. Barium titanate nanocatalysts had a 10.2 nm crystallite size without any impurities (Fig. 1b). The crystal structures were hardly changed by the CO<sub>2</sub> reduction reaction at 700 K and 0.01–1.0 MPa, although tiny amounts of impurities attributed to barium carbonate appeared by BaCO<sub>3</sub>-like structure formation on the nanocatalyst surface *via* CO<sub>2</sub> chemisorption. In our preceding report, we indicated that surface-chemisorbed CO<sub>2</sub> and reduced carbon would be released by preheating in the O<sub>2</sub> atmosphere and the catalytic activity would be recovered.<sup>36,38</sup> In addition, the crystal structure of nanocatalyst was maintained during heating. Meanwhile, a peak attributed to amorphous/graphitic carbons was hardly observed, whereas the phase periodicity of carbon is necessary for apparent diffraction to generate distinct XRD peaks.<sup>39</sup> On the other hand, sp<sup>2</sup> hybridized carbons could be identified by observing the D- and G-bands at 1300–1340 and 1600 cm<sup>-1</sup> in Raman spectra, respectively.<sup>40</sup>

Fig. 2 shows the Raman scattering spectra of the nanocatalysts after CO<sub>2</sub> thermolysis and the pristine nanocatalyst (see also in Fig. S2†). The barium titanate nanocatalysts originally had a peak at 1500 cm<sup>-1</sup>; thus, the peak intensities were normalized using the peak at 1500 cm<sup>-1</sup>. Additional peaks on the D- and G-bands were increasingly observed with higher-

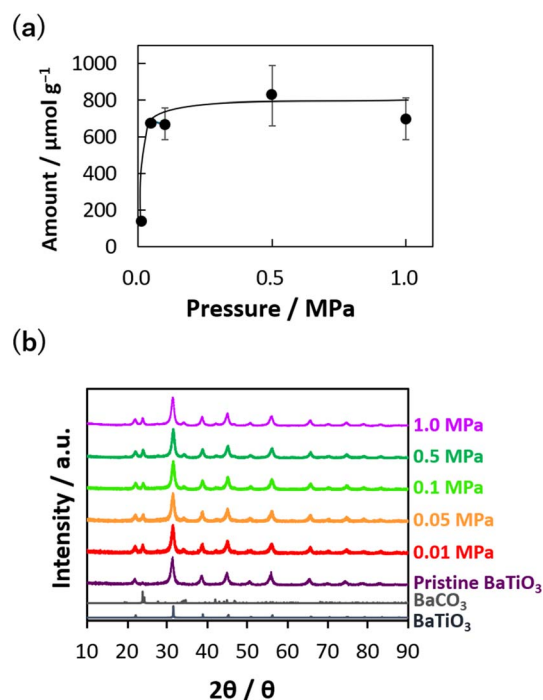


Fig. 1 (a) Weight increase of nanocatalysts after CO<sub>2</sub> thermolysis at 0.01–0.5 MPa. (b) XRD patterns of barium titanate nanocatalysts after CO<sub>2</sub> thermolysis. XRD patterns of barium carbonate and crystalline barium titanate are also shown as references.





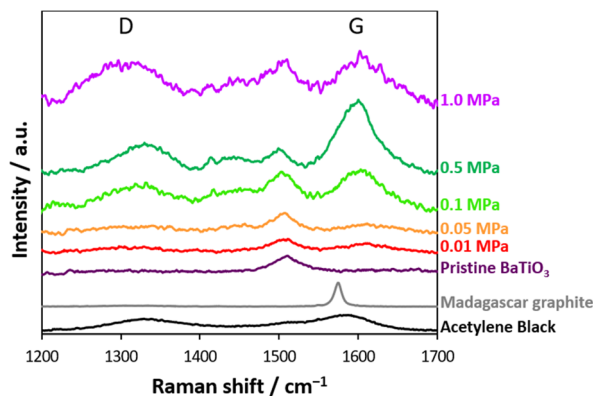


Fig. 2 Raman scattering spectra of the nanocatalysts before and after  $\text{CO}_2$  thermolysis. Raman scattering spectra of acetylene black and Madagascar graphite are shown for reference.

pressure treatment in  $\text{CO}_2$  thermolysis, accompanied by peak broadening. The Raman scattering spectra of typical carbons, such as acetylene black and Madagascar graphite, are also shown in Fig. 2. Acetylene black has distinctive D- and G-bands at  $1336$  and  $1592\text{ cm}^{-1}$ , respectively, as expected from a lack of well-defined structural order,<sup>41</sup> whereas Madagascar graphite has only G-band at  $1580\text{ cm}^{-1}$ . Ferrari and Robertson revealed that the G-band peak aligns with the in-plane bond stretching of  $\text{sp}^2$  C atom pairs, while the D-band peak is associated with the breathing modes of rings.<sup>42</sup> Defects such as vacancies and dislocations yield D-band peaks. Notably, the Raman scattering spectra of the nanocatalysts resembled that of less graphitized carbon, and the  $\text{CO}_2$ -reduced carbon amounts increased with reaction pressure. In addition, a broad peak that emerged in the range of  $1410\text{--}1460\text{ cm}^{-1}$  was observed for high-pressure  $\text{CO}_2$  thermolysis, associated with a defective D-band caused by structural anomalies.<sup>43,44</sup> The Raman scattering spectra at  $1400\text{--}1470\text{ cm}^{-1}$  were an indicator of structural disorder and defects in carbon materials.<sup>42,43</sup> We summarize the formation of carbon by  $\text{CO}_2$  thermolysis at different pressures. By  $\text{CO}_2$  thermolysis at  $0.01$  and  $0.05$  MPa, carbon structures were slightly observed, indicating slight/partial  $\text{CO}_2$  reduction. Graphitic carbons with disordered (amorphous) structures were observed at  $0.1$  and  $0.5$  MPa.<sup>43</sup> The disordered structures were significant after  $\text{CO}_2$  thermolysis at  $1.0$  MPa. This result indicated that high-pressure  $\text{CO}_2$  gas was reduced even on less active sites in a chain reaction.

The TEM images in Fig. 3 show carbon coating on particles of barium titanate nanocatalysts after  $\text{CO}_2$  thermolysis at  $700\text{ K}$  under pressures of  $0.01$ ,  $0.05$ ,  $0.1$ ,  $0.5$ , and  $1.0$  MPa for  $24\text{ h}$ . Carbon products resulting from  $\text{CO}_2$  reduction considerably increased with  $\text{CO}_2$  pressure, which was also expected from the optical color change from white to grayish-black.  $\text{CO}_2$  thermolysis at  $0.01$  MPa hardly produced carbons, whereas the TEM images above  $0.05$  MPa indicated catalytic reduction of  $\text{CO}_2$ , corresponding to the isothermal weight change analysis in Fig. 1a. The weight change observed in the low-pressure  $\text{CO}_2$  reactions was primarily attributed to chemisorbed  $\text{CO}_2$ , while chemisorbed  $\text{CO}_2$  was hardly observed in the TEM images in

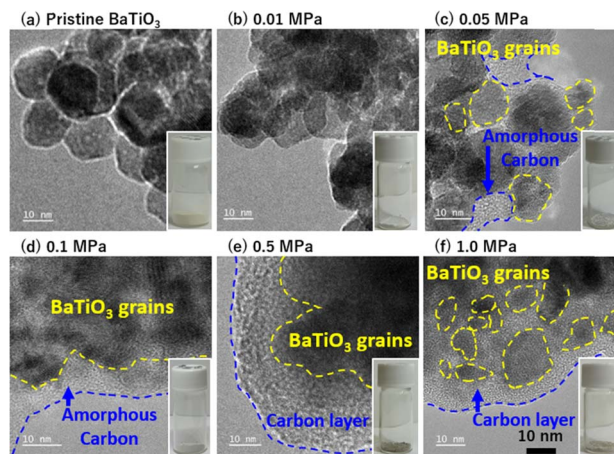


Fig. 3 TEM images of (a) pristine nanocatalyst and nanocatalyst after  $\text{CO}_2$  thermolysis at (b)  $0.01$ , (c)  $0.05$ , (d)  $0.1$ , (e)  $0.5$ , and (f)  $1.0$  MPa. The insets show the optical images of the nanocatalysts.

Fig. 3b. Reduced carbon was observed from  $0.05$  MPa in Fig. 3c. A large amount of carbon products was observed on the nanocatalysts after  $\text{CO}_2$  thermolysis above  $0.1$  MPa (Fig. 3d–f), reaching a detectable level of carbon deposited on nanocatalysts in Raman spectroscopy (Fig. 2).

The dependence of  $\text{CO}_2$  thermolysis duration was also examined for  $\text{CO}_2$  thermolysis at  $0.5$  MPa, which was the best pressure condition for producing graphitic carbon (Fig. 2). The reduced carbon attached to the nanocatalysts after  $\text{CO}_2$  thermolysis was quantitatively analyzed by the TGA; the amount after thermolysis at  $0.5$  MPa for  $1$ ,  $5$ , and  $10$  days were  $830 \pm 160$ ,  $1060$ , and  $1450\text{ }\mu\text{mol g}^{-1}$ , respectively. Fig. 4a shows the XRD patterns of the nanocatalysts after  $\text{CO}_2$  thermolysis. The

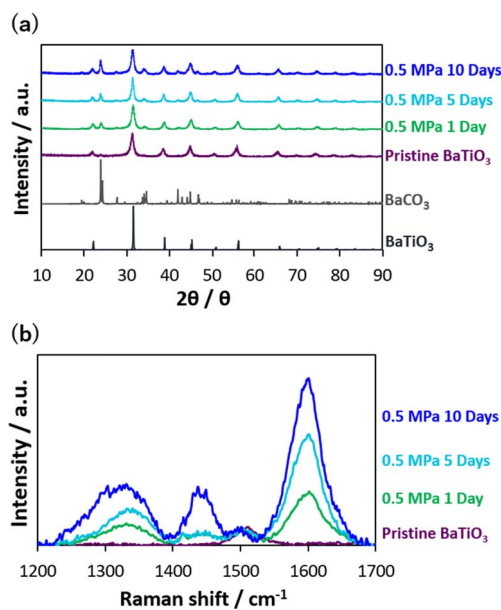


Fig. 4 (a) XRD of nanocatalysts at  $700\text{ K}$  and  $0.5$  MPa for  $1\text{--}10$  days. (b) Raman spectra of pristine barium titanate and nanocatalysts after  $\text{CO}_2$  thermolysis.



nanocatalyst structures hardly changed, while  $\text{BaCO}_3$  peaks appeared increasingly, probably due to surface carbonate formation on the Ba sites. Crystalline and amorphous graphitic structures were also observed in the Raman scattering spectra (Fig. 4b); D-, defective D-, and G-bands increased with heating duration in  $\text{CO}_2$  thermolysis. Graphitic carbons mostly increased, because of an increase in the G-band intensity.

Fig. 5 shows carbon removal from nanocatalysts after  $\text{CO}_2$  thermolysis by  $\text{CO}_2$ -TPD-mass spectra in an  $\text{O}_2$  atmosphere in which  $\text{CO}_2$  was produced on nanocatalysts with carbons by oxidation. Carbon structures were thus assessed from distinctive temperatures during TPD measurements.<sup>45</sup> The  $\text{CO}_2$ -TPD-mass spectra of acetylene black and Madagascar graphite are shown in Fig. S3.† Broad  $\text{CO}_2$  peaks on carbon materials appeared at 400 K, probably due to the removal of surface oxygen groups, which were also observed elsewhere.<sup>46–49</sup> The oxidation temperature of carbon materials associated with the strong, sharp peaks indicated that less- and high-crystalline carbons were oxidized at 1000 and 1270 K, respectively. The nanocatalysts after  $\text{CO}_2$  thermolysis at 0.01 MPa, as well as the pristine nanocatalyst, had no  $\text{CO}_2$  peak, indicating no detectable level of  $\text{CO}_2$  reduction. Meanwhile,  $\text{CO}_2$  mass peaks were observed for nanocatalysts above 0.05 MPa. The  $\text{CO}_2$  peak between 300–500 K was due to the desorption of chemisorbed  $\text{CO}_2$  on the nanocatalyst surface. Carbon dioxide evolved at 800–900 K and slightly at 900–1100 K for the nanocatalysts at 0.05 MPa, in which amorphous and graphitic carbons on the nanocatalysts were oxidized, respectively. Here, oxidation of typical carbon materials is observed in the range of 600–700 K for activated carbons, 900–1100 K for graphitized carbon, and 500–1100 K for high-surface-area graphite, polycrystalline graphite, nonporous carbon, and diamond powders.<sup>46,47,50–54</sup> Chemisorbed  $\text{CO}_2$  peaks were also observed for the nanocatalysts above 0.1 MPa, while  $\text{CO}_2$  peaks by the oxidation of amorphous carbons between 800 and 900 K were weakened, and alternatively, the peaks by the oxidation of graphitic carbons above 900 K were distinct. This was expected based on the Raman spectra shown in Fig. 2. Therefore, various carbon structures were formed on the nanocatalysts after  $\text{CO}_2$

thermolysis. Previous studies also indicated graphitic carbons on Pt/ $\text{TiO}_2$  and Ru/ $\text{TiO}_2$  catalysts,<sup>55</sup> filamentous carbons on Pt/MgO– $\text{Al}_2\text{O}_3$  catalysts, Ru support on modified  $\text{SiO}_2$  catalysts, and Rh/ $\gamma\text{-Al}_2\text{O}_3$ – $\text{La}_2\text{O}_3$  catalysts.<sup>56–58</sup> Ghelamallah and Grangers identified four types of carbon on Rh/ $\text{La}_2\text{O}_3$ ; the  $\text{CO}_2$  peaks below 523 K, within 635–661 K, within 693–798 K, and above 973 K demonstrated weakly bound carbon deposited directly on the rhodium metal, carbons at the boundary between the metal and lanthanum oxide support, carbons on the lanthanum oxide, and graphitic carbon, respectively.<sup>59</sup> This indicated that the nanocatalysts had strong  $\text{CO}_2$  reduction activity, assumed from graphitic carbon production, which was evaluated by the high-temperature oxidation of carbons above 900 K. The heating duration during  $\text{CO}_2$  thermolysis also influenced the carbon structure of the nanocatalysts, as evaluated from the  $\text{CO}_2$ -TPD-mass spectra in Fig. 5. The oxidation peak for the 0.5 MPa-based  $\text{CO}_2$  thermolysis at 1050 K was intense in five days and was split into two peaks at 1000 and 1150 K in ten days. Graphitic carbon changed to less- and higher-crystalline graphitic carbons during long-term  $\text{CO}_2$  thermolysis by aging associated with crystal growth of carbons and remained amorphous region.

The possible reaction mechanism for  $\text{CO}_2$  reduction on the nanocatalysts may originate from  $\text{CO}_2$  chemisorption onto an active metal surface to the dissociation of carbon dioxide to carbon monoxide ( $2\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_{2(\text{g})}$ ) and then further reaction to solid carbon with reduction and a disproportionation reaction ( $2\text{CO} \rightarrow \text{C}_{(\text{s})} + \frac{1}{2}\text{O}_{2(\text{g})}$  and  $2\text{CO} \rightarrow \text{C}_{(\text{s})} + \text{CO}_{2(\text{g})}$ ), although  $\text{O}_2$  production was not detected in the TPD. A high temperature is normally required for the exothermic reduction reactions, but the above reduction reactions of  $\text{CO}_2$  and CO on the nanocatalysts are promoted at higher pressure by Le Chatelier's principle. On the other hand, the disproportionation reaction promotes carbon solidification ( $2\text{CO} \rightarrow \text{C}_{(\text{s})} + \text{CO}_{2(\text{g})}$ ) at temperatures lower than 900 K. Therefore, superior  $\text{CO}_2$  reduction activity on barium titanate nanocatalysts at 700 K facilitated further reduction to solid carbons.

## Conclusions

In this study,  $\text{CO}_2$  conversion into solid carbons using barium titanate nanocatalysts at 700 K and various pressures was demonstrated to reveal the unique reaction mechanism and pressure dependence of  $\text{CO}_2$  thermolysis. The nanocatalysts facilitated  $\text{CO}_2$  reduction to amorphous and graphitic carbons at 700 K and high pressure, especially at 0.1–0.5 MPa, where a greater amount of reduced carbon was observed from TEM and optical images, Raman scattering spectroscopies, and TPD-Mass analyses of the nanocatalysts after  $\text{CO}_2$  thermolysis reaction. The findings of this study indicated that  $\text{CO}_2$  reduction to CO on the nanocatalysts facilitated further reduction to graphitic carbon at high pressures, even at 700 K. This knowledge is essential for optimizing reaction conditions and maximizing  $\text{CO}_2$  conversion efficiency using more sustainable technology. However, further investigations are required to evaluate the  $\text{CO}_2$  reduction mechanism associated with theoretical analyses in order to develop highly active  $\text{CO}_2$  reduction catalysts.

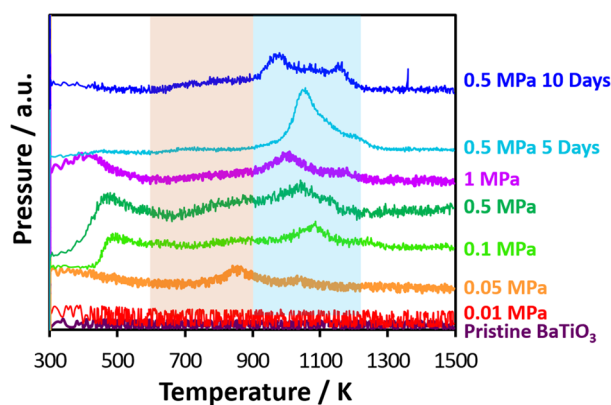


Fig. 5 TPD spectra of  $\text{CO}_2$ -reduced carbons on nanocatalysts in  $\text{O}_2$  atmosphere after  $\text{CO}_2$  thermolysis at 0.01, 0.05, 0.1, 0.5, and 1.0 MPa for one day and 0.5 MPa for five and ten days.



## Data availability

The data supporting this article have been included as part of the ESI.† The data that support the findings of this study are available from the corresponding author, T. O., upon reasonable request.

## Author contributions

ST: methodology, investigation, analyzing the data, writing the original draft of the manuscript; MM: analyzing the data; TW: methodology; TO: supervision, conceptualization, writing, reviewing, and editing.

## Conflicts of interest

There are no conflicts to declare.

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