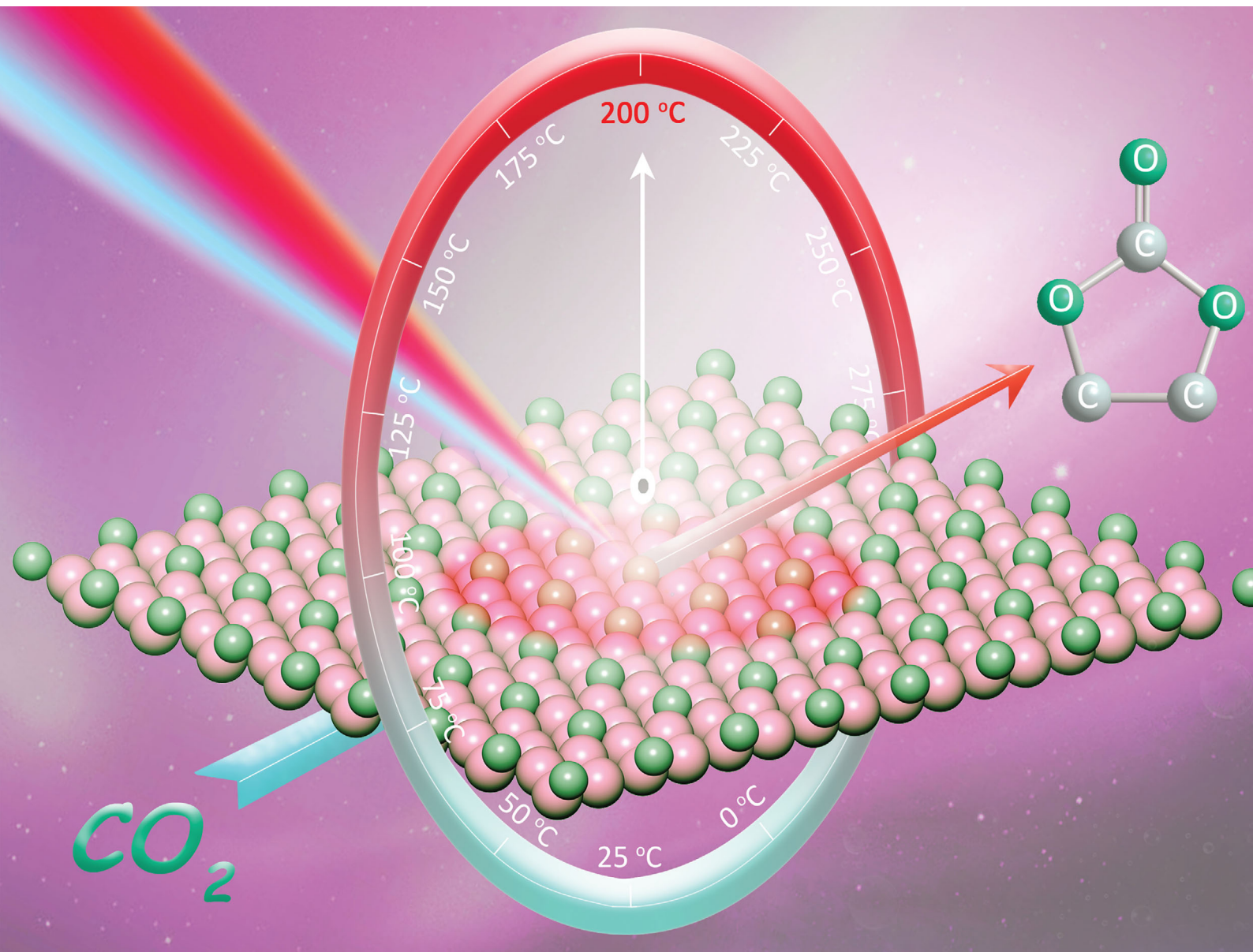


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conversion



# Flower-like cobalt carbide for efficient carbon dioxide conversion†

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**Catalytic conversion of carbon dioxide (CO<sub>2</sub>) to value-added chemicals under mild conditions is highly desired, albeit with significant challenges. Here, in terms of exposure of abundant active sites and excellent photo-to-thermal conversion properties, flower-like Co<sub>2</sub>C has been firstly used for effectively catalysing the cycloaddition of CO<sub>2</sub> with epoxides to produce cyclic carbonates with yields of up to 95% under solar light. Density functional theory (DFT) calculations reveal that Lewis acid sites of the surface Co atoms can activate both CO<sub>2</sub> and epoxide, thus opening up the possibility of a CO<sub>2</sub>-epoxide cycloaddition reaction.**

The increasing atmospheric concentration of carbon dioxide (CO<sub>2</sub>), which is regarded as the main greenhouse gas, has caused serious environmental concerns (*e.g.*, global warming, abnormal climate change and sea level rise).<sup>1–4</sup> To address the anthropogenic CO<sub>2</sub> emission issues,<sup>5–11</sup> the approaches of physical CO<sub>2</sub> capture and storage,<sup>12,13</sup> and chemical conversion of CO<sub>2</sub> into usable fuels and/or value-added chemicals<sup>14,15</sup> have been widely investigated. From a chemical point of view, cycloaddition of CO<sub>2</sub> with epoxides represents one of the most promising strategies to generate valuable chemicals.<sup>16–18</sup> By using CO<sub>2</sub> as the renewable and nontoxic one-carbon (C<sub>1</sub>) feedstock,<sup>19</sup> cyclic carbonates are produced with 100% atom-economy efficiency.<sup>20</sup> Cyclic carbonates can be directly employed in industry as solvents or intermediates, such as carbamates,<sup>21</sup> polycarbonates<sup>22</sup> and spiro compounds.<sup>23</sup> Numerous advances in homogeneous (*e.g.*, Co,<sup>24,25</sup> Ni,<sup>26</sup> Al<sup>27</sup> and Cu-based<sup>28</sup> monometallic or bimetallic complexes) and heterogeneous (*e.g.*, metal-organic-frameworks (MOFs),<sup>29–31</sup> mesoporous

polymers,<sup>32</sup> and zeolites<sup>33</sup>) catalysts have been made for the cycloaddition of CO<sub>2</sub> with epoxides. However, most of the state-of-the-art catalysts can work fairly well to yield cyclic carbonates only at an elevated temperature, thus leading to an increase of the energy cost.

Transition-metal carbides (TMCs) show great potential in the field of catalysis owing to their outstanding electronic conductivity, good chemical stability, abundant surface active sites and high photo-to-thermal conversion efficiency.<sup>34–36</sup> Cobalt carbide (Co<sub>2</sub>C), for example, has been demonstrated to be an effective catalyst in various transformations (*e.g.*, hydrogen evolution and Fischer–Tropsch synthesis).<sup>37,38</sup> However, the application of cobalt carbide in cycloaddition of CO<sub>2</sub> with epoxides is still elusive. Considering these attributes, we are inspired to explore Co<sub>2</sub>C as a novel catalyst for cycloaddition of CO<sub>2</sub> with epoxides by using solar energy to replace external thermal energy input for following reasons: (i) the high specific surface area and tuneable chemical composition provide abundant surface active sites to activate CO<sub>2</sub> and/or epoxides; (ii) the effective CO<sub>2</sub> adsorption ability on TMCs favours the very first step of CO<sub>2</sub> conversion;<sup>39</sup> (iii) the huge amount of heat released during the excellent photo-to-thermal conversion process would promote the endothermic reaction (high C=O bond energy of 750 kJ mol<sup>−1</sup>);<sup>40</sup> and (iv) the feasible separation and reusability of the heterogeneous catalysts is beneficial for large-scale applications.<sup>41</sup> To our delight, flower-like Co<sub>2</sub>C facilitates the catalysis of CO<sub>2</sub>-epoxide cycloaddition with yields of up to ~95% under visible light (Scheme 1), showing the first example of using TMCs for photothermal-driven CO<sub>2</sub> conversion.

Flower-like Co<sub>2</sub>C was synthesized through a modified method of solution pyrolysis at high temperature (Fig. 1a),<sup>42–44</sup> see experimental details in the ESI.† Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) clearly showed the flower-like morphology of the synthesized material (Fig. 1b and c). The average diameter of the nanoflowers was determined to be ~500 nm by TEM characterization (Fig. 1c). The nearly apparent nanosheet on the outside of the nanoflowers indicated that the obtained nanoflower was a result of self-assembly of

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**Scheme 1** Illustration of the photothermal-driven cycloaddition of  $\text{CO}_2$  with epoxides catalyzed by  $\text{Co}_2\text{C}$  nanosheets of the nanoflower.



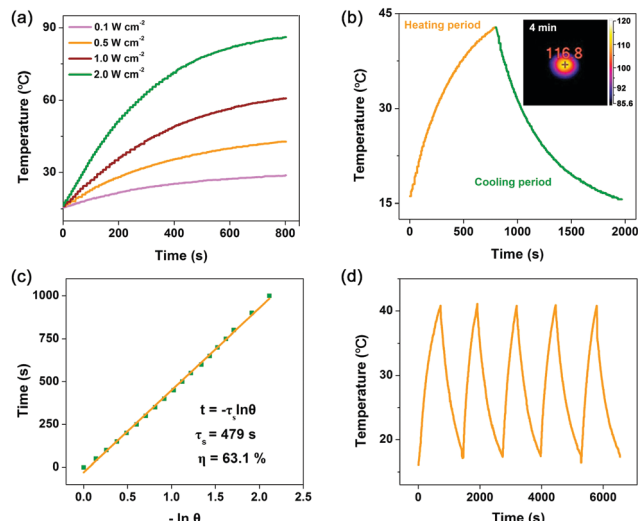
**Fig. 1** (a) Synthetic process of flower-like  $\text{Co}_2\text{C}$ . (b) SEM image (the inset panel is the high-resolution SEM image) and (c) TEM image of  $\text{Co}_2\text{C}$  nanoflowers. (d) High-resolution TEM image of  $\text{Co}_2\text{C}$  (the inset panel is the corresponding SAED pattern). (e) The corresponding lattice distances of the exposed (101) plane of  $\text{Co}_2\text{C}$ . (f) XRD pattern and (g) C 1s XPS spectrum of  $\text{Co}_2\text{C}$  nanoflowers. (h) Magnitude of  $k^2$ -weighted Fourier transform of the Co K-edge EXAFS spectra of Co foil and the obtained  $\text{Co}_2\text{C}$  nanoflowers with corresponding curve-fitting results.

individual nanosheets. The thickness of individual nanosheet was determined to be  $\sim 2.4$  nm by atomic force microscopy (AFM) (Fig. S1, ESI<sup>†</sup>). In the high-resolution TEM image, a lattice distance of  $\sim 2.41$  Å was observed, indicating the exposure of the (101) facet of  $\text{Co}_2\text{C}$  (Fig. 1d and e). Moreover, selective area electron diffraction (SAED) patterns in Fig. 1d confirmed the polycrystalline nature of the synthesized materials. In addition, elemental mapping analysis indicated the coexistence of Co, C and O elements (Fig. S2, ESI<sup>†</sup>), which matched well with the X-ray photoelectron spectroscopy (XPS) results (see below).

The powder X-ray diffraction (XRD) (Fig. 1f) pattern of the as-prepared sample was in good agreement with the standard pattern of  $\text{Co}_2\text{C}$  (Joint Committee on Powder Diffraction Standards (JCPDS) Powder Diffraction File (PDF) No. 65-1457),<sup>42</sup> indicating the successful formation of  $\text{Co}_2\text{C}$ . The peaks at 1630, 1420 and  $1050\text{ cm}^{-1}$  corresponding to C=C, C-H, and C-N bonds, respectively, in the Fourier transform infrared (FTIR) spectra (Fig. S3, ESI<sup>†</sup>) almost disappeared after calcination, suggesting the removal of surface organic ligands. Full XPS survey confirmed the coexistence of Co, C and O elements in the obtained sample (Fig. S4, ESI<sup>†</sup>). High-resolution XPS spectra of C 1s (Fig. 1g) and Co 2p (Fig. S5, ESI<sup>†</sup>) show the characteristic peaks of carbide and carbidic Co at 282.7 and 778.1 eV,<sup>36,45,46</sup> respectively. Combined with the peak at 531.6 eV in the O 1s XPS spectrum (Fig. S6, ESI<sup>†</sup>), the peak at 781.0 eV in the Co 2p XPS spectrum was attributed to the  $\text{Co}(\text{OH})_2$  species formed in the process of  $\text{Co}_2\text{C}$  preparation, proving the fact that solution pyrolysis under high temperature inevitably leads to the formation of trace amounts of the hydroxide impurity.<sup>46,47</sup> Fig. 1h shows the X-ray absorption spectra (XAS) of the obtained sample. The Co K-edge extended X-ray absorption fine structure (EXAFS) of the synthesized sample exhibits two peaks in the  $R$ -space, which could be assigned to the first Co-C shell (1.89 Å) and the second Co-Co shell (2.54 Å) of  $\text{Co}_2\text{C}$ , see the fitting details in Table S1, ESI<sup>†</sup>.

Then, photo-to-thermal conversion effects of  $\text{Co}_2\text{C}$  nanoflowers were experimentally examined. UV-vis-NIR diffuse reflectance spectroscopy (DRS) measurement indicated that the synthesized  $\text{Co}_2\text{C}$  nanoflowers showed strong absorption in the range of 300 to 1200 nm (Fig. S7, ESI<sup>†</sup>), directly confirming its excellent light-harvesting properties. When the water suspension of  $\text{Co}_2\text{C}$  nanoflowers ( $0.6\text{ mg mL}^{-1}$ ) was exposed to a 635 nm laser at varied power densities ( $0.1, 0.5, 1.0$  and  $2.0\text{ W cm}^{-2}$ ), the solution displayed apparent temperature elevation (Fig. 2a). For instance, under 635 nm laser irradiation ( $0.5\text{ W cm}^{-2}$ ), the temperature of the  $\text{Co}_2\text{C}$  nanoflowers water suspension reached  $42.8^\circ\text{C}$  in 13 minutes, while the temperature of pure water only increased to  $24^\circ\text{C}$  under the same conditions (Fig. S8, ESI<sup>†</sup>). Huge amount of heat released from  $\text{Co}_2\text{C}$  nanoflowers was also monitored by an IR camera in the solid state. As shown in the inset panel of Fig. 2b, the local temperature of the powder  $\text{Co}_2\text{C}$  sample quickly increased to  $116.8^\circ\text{C}$  upon exposure to a 635 nm laser ( $0.5\text{ W cm}^{-2}$ ) for 4.0 min, further confirming the *in situ* conversion of solar light into heat.

On the basis of the time constant for heat transfer and the maximal steady-state temperature, photo-to-thermal conversion efficiency ( $\eta$ ), regarded as a major parameter in evaluating the performance in converting light to heat of a given material,<sup>48</sup> of the flower-like  $\text{Co}_2\text{C}$  was calculated to be as high as  $\sim 63.1\%$  at 635 nm (Fig. 2b and c, see details in the ESI<sup>†</sup>). The exceptional photo-to-thermal conversion performance of  $\text{Co}_2\text{C}$  nanoflowers obtained here was comparable with those of the reported materials (Table S2, ESI<sup>†</sup>). To further evaluate its photothermal stability, temperature variations of  $\text{Co}_2\text{C}$  nanoflowers suspension were recorded under light irradiation (laser on) followed by natural cooling to room temperature (laser off). As shown in Fig. 2d,



**Fig. 2** (a) Photothermal heating curves of Co<sub>2</sub>C nanoflowers dispersed in water under 635 nm laser irradiation at varied power densities (0.1, 0.5, 1.0 and 2.0 W cm<sup>-2</sup>). (b) Photothermal effect of Co<sub>2</sub>C aqueous dispersion under 635 nm laser irradiation (0.5 W cm<sup>-2</sup>) and the cooling process after laser off. The inset panel in (b) is the IR image of Co<sub>2</sub>C powder under 635 nm laser irradiation (0.5 W cm<sup>-2</sup>) for 4.0 min. (c) The corresponding time constant (τ<sub>s</sub>) for the heat transfer from the system determined by applying the linear time data from cooling period. (d) Recycling-heating curves of the Co<sub>2</sub>C aqueous suspension with 635 nm laser irradiation at 0.5 W cm<sup>-2</sup> for five laser on/off cycles.

negligible changes in temperature elevation were observed during 5 cycles, which highlighted the potential application of Co<sub>2</sub>C nanoflowers as durable photothermal materials.

To investigate the catalytic performance of Co<sub>2</sub>C nanoflowers, 3-chloropropylene oxide was chosen as the model substrate under visible light (Table 1). A water/fan-cooling system was employed to maintain the outside temperature of the reactor at room temperature, see experimental details in the ESI†. Increase of Co<sub>2</sub>C nanoflowers from 0 to 25 mg obviously improved the yields up to ~93.5% (entries 1–4; Table 1). Control experiments showed that all components were essential for the conversion. Trace or negligible amount of the product was detected without light, tetrabutylammonium bromide (TBAB) or CO<sub>2</sub> (entries 5–7; Table 1). When tetrabutylammonium chloride (TBAC) was employed as the co-catalyst, a significantly declined yield of ~27% was observed (entry 8; Table 1). This result showed that easier dissociation and stronger nucleophilicity of Br<sup>-</sup> compared to Cl<sup>-</sup> dramatically benefited the ring-opening reaction of epoxides.<sup>29</sup> To verify the photothermal effects of Co<sub>2</sub>C nanoflowers, we monitored the temperature variation of the reaction solution by using a thermometer. Upon light irradiation, the temperature of the solution was significantly elevated to ~60 °C in a period of 35 min (Fig. S9, ESI†), indicating the conversion of light into heat. Moreover, very similar yields were observed under either visible-light irradiation or external heating (60 °C), implying that the photothermal effects could promote the cycloaddition reaction between CO<sub>2</sub> and epoxide (Fig. S10, ESI†).

Furthermore, the obtained Co<sub>2</sub>C sample was treated with hydrochloric acid (HCl; 6 mol L<sup>-1</sup>) to exclude the contribution

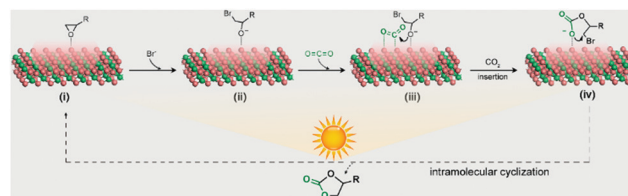
**Table 1** Optimization of the reaction conditions<sup>a</sup>

Entry	Catalyst	Additive	Yield <sup>b</sup> (%)
1	Co <sub>2</sub> C (0 mg)	TBAB	< 5
2	Co <sub>2</sub> C (15 mg) <sup>c</sup>	TBAB	54
3	Co <sub>2</sub> C (15 mg)	TBAB	73.3
4	Co <sub>2</sub> C (25 mg)	TBAB	93.5
5	Co <sub>2</sub> C (25 mg) <sup>d</sup>	TBAB	< 5
6	Co <sub>2</sub> C (25 mg)	—	0
7	Co <sub>2</sub> C (25 mg) <sup>e</sup>	TBAB	0
8	Co <sub>2</sub> C (15 mg) <sup>f</sup>	TBAC	26.7
9	Co <sub>2</sub> C (25 mg) <sup>g</sup>	TBAB	81.9
10	Co(OH) <sub>2</sub> (25 mg)	TBAB	64
11	CoO (25 mg)	TBAB	63.6
12	Co <sub>3</sub> O <sub>4</sub> (25 mg)	TBAB	48.6
13	Co <sub>2</sub> C (50 mg) <sup>h</sup>	TBAB	66.4

<sup>a</sup> Reaction conditions: 0.15 mmol 3-chloropropylene oxide, 0.25 mmol TBAB, 3 mL CH<sub>3</sub>CN as the solvent, blue LEDs (λ = 450 nm) as the light source, 15 h. <sup>b</sup> The carbonate product was quantified by <sup>1</sup>H NMR with diphenylmethanol as the internal standard. The yield was calculated by the equation, [η (%) = n(carbonate)/n(3-chloropropylene oxide) × 100%]. <sup>c</sup> 0.1 mmol TBAB. <sup>d</sup> No light irradiation. <sup>e</sup> N<sub>2</sub> instead of CO<sub>2</sub>. <sup>f</sup> 0.1 mmol TBAC. <sup>g</sup> Co<sub>2</sub>C nanoflowers treated with HCl (6 mol L<sup>-1</sup>). <sup>h</sup> 0.50 mmol TBAB, AM 1.5 (100 mW cm<sup>-2</sup>) as the light source, 24 h.

of trace amounts of cobalt hydroxide (*i.e.*, Co(OH)<sub>2</sub>) and/or cobalt oxide (*i.e.*, CoO and Co<sub>3</sub>O<sub>4</sub>) on the surface of Co<sub>2</sub>C nanoflowers in CO<sub>2</sub> fixation. After treating the sample with HCl, the slightly declined yield of the target product was still much higher than those of pure Co(OH)<sub>2</sub>, CoO, or Co<sub>3</sub>O<sub>4</sub> under the same conditions (entries 9–12; Table 1). These results confirmed that Co<sub>2</sub>C, but not the hydroxide or oxide impurities, served as the real active sites for CO<sub>2</sub> fixation. More importantly, the Co<sub>2</sub>C catalysed cycloaddition reaction of CO<sub>2</sub> and epoxides with electron-donating/withdrawing groups could also give rise to products in good to excellent yields (~95%) (Table S3, ESI†). Even under AM1.5 irradiation (entry 13; Table 1), this reaction proceeded with good yields. The activity was well preserved after three-time recycling (Fig. S11, ESI†), indicating the potential use of sunlight as the energy source for enhanced photothermal catalysis.

Based on the above experimental results, a plausible mechanism of the Co<sub>2</sub>C nanoflowers catalysed CO<sub>2</sub>-epoxide cycloaddition reaction is proposed (Fig. 3). Epoxide molecules adsorb on the surface exposed Co sites *via* Co–O interaction with an adsorption energy of –0.53 eV (Fig. S12a, see details of density functional theory (DFT) calculations in the ESI†), thereby



**Fig. 3** The proposed mechanism of Co<sub>2</sub>C catalysed CO<sub>2</sub> cycloaddition with epoxides under light irradiation.

leading to the elongation of C–O bond from 1.956 to 2.086 Å. Then, the nucleophilic Br<sup>−</sup> ion attacks the adsorbed epoxide at the less hindered carbon atom to generate the metal alkoxide intermediate *via* the ring-opening reaction. At the same time, CO<sub>2</sub> adsorbs on the surface Co atom to give a bent molecular configuration (O1–C–O2 angle 146.99°) with a concerted interaction of C–Co and O–Co coordination (Fig. S12b, ESI†). With the aid of photothermal Co<sub>2</sub>C nanoflowers, the oxygen anion of the alkoxide intermediate combines with the adjacent highly activated CO<sub>2</sub> molecules to yield the cyclic carbonate product, which is eventually released into the solvent to regenerate the catalyst. As a huge amount of heat is released due to the excellent photo-to-thermal conversion effects of Co<sub>2</sub>C, the endothermic CO<sub>2</sub> cycloaddition reaction proceeds with high yields, which is comparable with the reported results (Table S4, ESI†).

In summary, an efficient CO<sub>2</sub> cycloaddition reaction with epoxides is achieved on low-priced photothermal catalyst of Co<sub>2</sub>C nanoflowers. The yield of cyclic carbonates is up to ~95% with visible-light irradiation, owing to the excellent photothermal effects of Co<sub>2</sub>C nanoflowers in converting light to heat. Besides, the high specific area as well as efficient CO<sub>2</sub> adsorption on the exposed Co atoms of the catalysts can simultaneously activate the adsorbed CO<sub>2</sub> and epoxides, thus promoting the CO<sub>2</sub> fixation reaction. This work provides new insights into the utilization of TMCs in the field of advanced photothermal-driven catalysis. Moreover, the influence of the morphology, size and thickness of TMCs on the catalytic performance will be further investigated by us.

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## Conflicts of interest

There are no conflicts to declare.

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