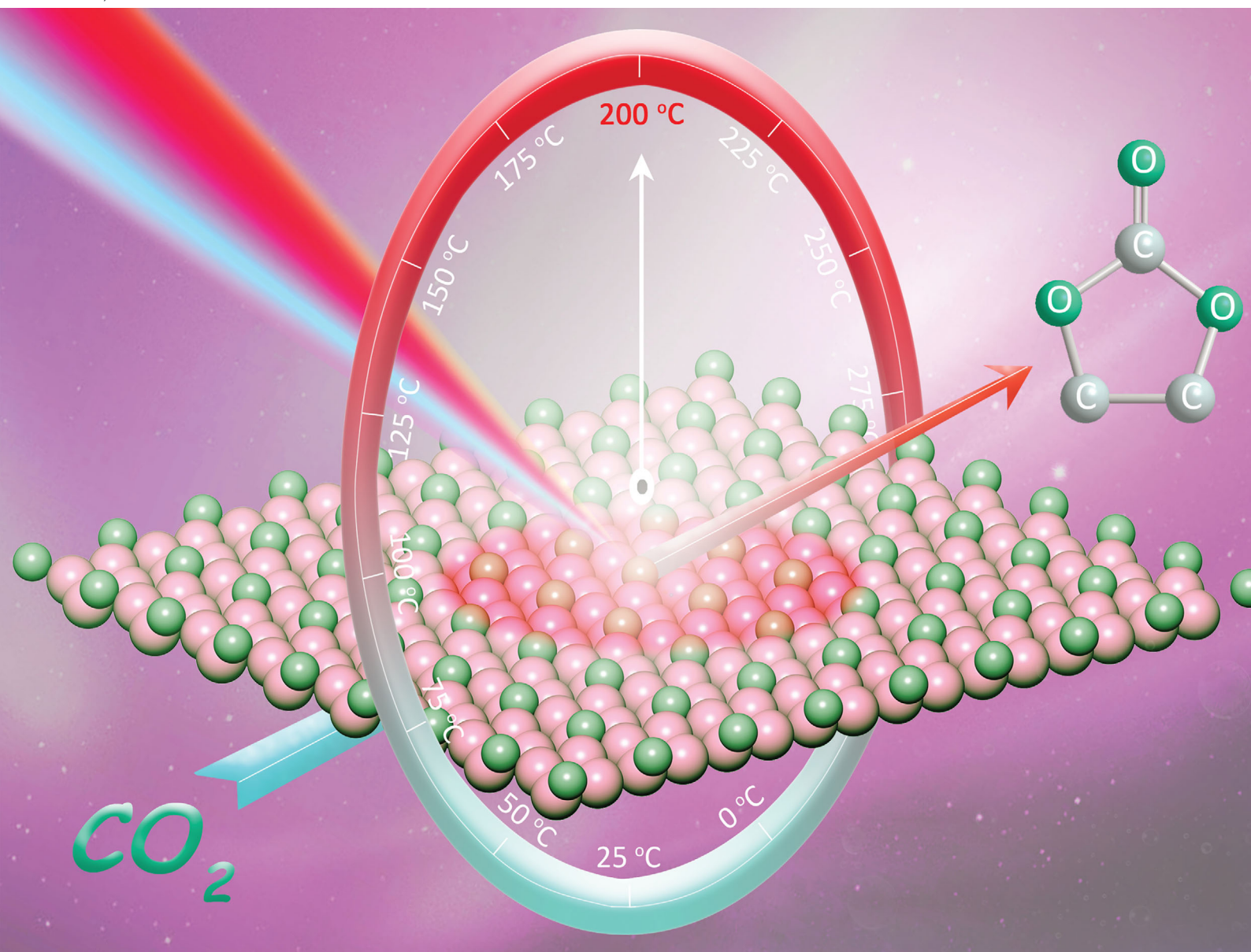


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Flower-like cobalt carbide for efficient carbon dioxide  
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# Flower-like cobalt carbide for efficient carbon dioxide conversion†

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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

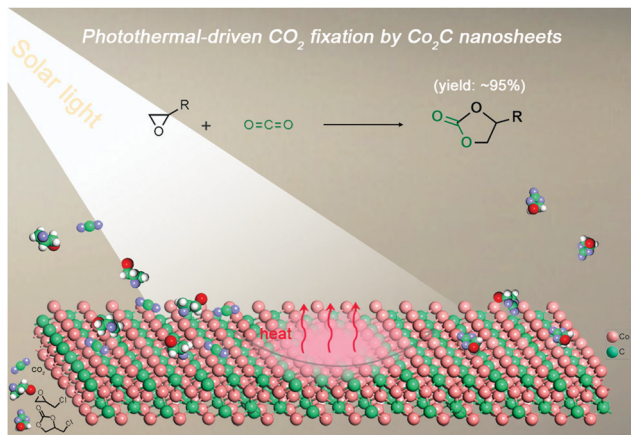
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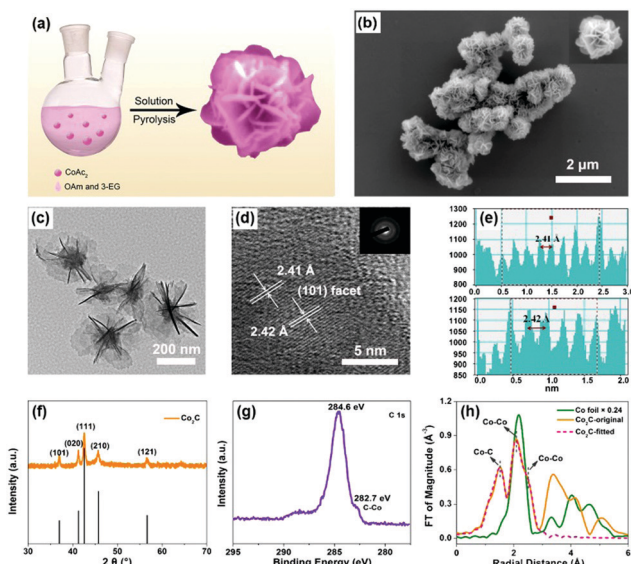
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‡ These authors contributed equally to this work.



**Scheme 1** Illustration of the photothermal-driven cycloaddition of CO<sub>2</sub> with epoxides catalyzed by Co<sub>2</sub>C nanosheets of the nanoflower.



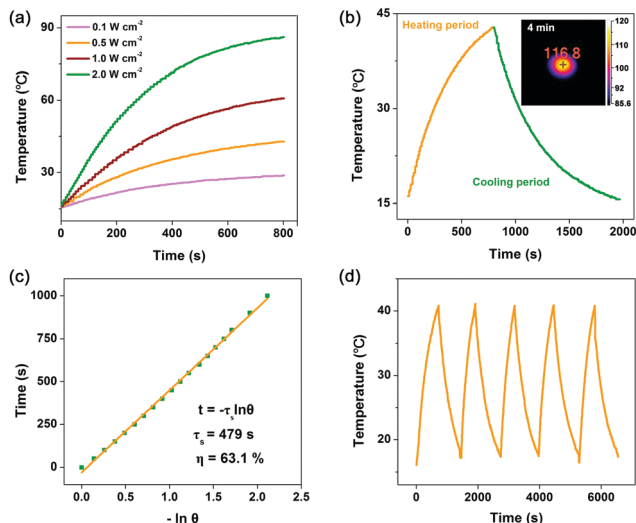
**Fig. 1** (a) Synthetic process of flower-like Co<sub>2</sub>C. (b) SEM image (the inset panel is the high-resolution SEM image) and (c) TEM image of Co<sub>2</sub>C nanoflowers. (d) High-resolution TEM image of Co<sub>2</sub>C (the inset panel is the corresponding SAED pattern). (e) The corresponding lattice distances of the exposed (101) plane of Co<sub>2</sub>C. (f) XRD pattern and (g) C 1s XPS spectrum of Co<sub>2</sub>C nanoflowers. (h) Magnitude of  $k^2$ -weighted Fourier transform of the Co K-edge EXAFS spectra of Co foil and the obtained Co<sub>2</sub>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 Co<sub>2</sub>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 Co<sub>2</sub>C (Joint Committee on Powder Diffraction Standards (JCPDS) Powder Diffraction File (PDF) No. 65-1457),<sup>42</sup> indicating the successful formation of Co<sub>2</sub>C. The peaks at 1630, 1420 and 1050 cm<sup>-1</sup> 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 Co(OH)<sub>2</sub> species formed in the process of Co<sub>2</sub>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 Co<sub>2</sub>C, see the fitting details in Table S1, ESI<sup>†</sup>.

Then, photo-to-thermal conversion effects of Co<sub>2</sub>C nanoflowers were experimentally examined. UV-vis-NIR diffuse reflectance spectroscopy (DRS) measurement indicated that the synthesized Co<sub>2</sub>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 Co<sub>2</sub>C nanoflowers (0.6 mg mL<sup>-1</sup>) was exposed to a 635 nm laser at varied power densities (0.1, 0.5, 1.0 and 2.0 W cm<sup>-2</sup>), the solution displayed apparent temperature elevation (Fig. 2a). For instance, under 635 nm laser irradiation (0.5 W cm<sup>-2</sup>), the temperature of the Co<sub>2</sub>C nanoflowers water suspension reached 42.8 °C in 13 minutes, while the temperature of pure water only increased to 24 °C under the same conditions (Fig. S8, ESI<sup>†</sup>). Huge amount of heat released from Co<sub>2</sub>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 Co<sub>2</sub>C sample quickly increased to 116.8 °C upon exposure to a 635 nm laser (0.5 W cm<sup>-2</sup>) 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 Co<sub>2</sub>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 Co<sub>2</sub>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 Co<sub>2</sub>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  $\text{Co}_2\text{C}$  nanoflowers dispersed in water under 635 nm laser irradiation at varied power densities (0.1, 0.5, 1.0 and 2.0  $\text{W cm}^{-2}$ ). (b) Photothermal effect of  $\text{Co}_2\text{C}$  aqueous dispersion under 635 nm laser irradiation (0.5  $\text{W cm}^{-2}$ ) and the cooling process after laser off. The inset panel in (b) is the IR image of  $\text{Co}_2\text{C}$  powder under 635 nm laser irradiation (0.5  $\text{W cm}^{-2}$ ) for 4.0 min. (c) The corresponding time constant ( $\tau_s$ ) for the heat transfer from the system determined by applying the linear time data from cooling period. (d) Recycling-heating curves of the  $\text{Co}_2\text{C}$  aqueous suspension with 635 nm laser irradiation at 0.5  $\text{W cm}^{-2}$  for five laser on/off cycles.

negligible changes in temperature elevation were observed during 5 cycles, which highlighted the potential application of  $\text{Co}_2\text{C}$  nanoflowers as durable photothermal materials.

To investigate the catalytic performance of  $\text{Co}_2\text{C}$  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  $\text{Co}_2\text{C}$  nanoflowers from 0 to 25 mg obviously improved the yields up to  $\sim 93.5\%$  (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  $\text{CO}_2$  (entries 5–7; Table 1). When tetrabutylammonium chloride (TBAC) was employed as the co-catalyst, a significantly declined yield of  $\sim 27\%$  was observed (entry 8; Table 1). This result showed that easier dissociation and stronger nucleophilicity of  $\text{Br}^-$  compared to  $\text{Cl}^-$  dramatically benefited the ring-opening reaction of epoxides.<sup>29</sup> To verify the photothermal effects of  $\text{Co}_2\text{C}$  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  $\sim 60^\circ\text{C}$  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 ( $60^\circ\text{C}$ ), implying that the photothermal effects could promote the cycloaddition reaction between  $\text{CO}_2$  and epoxide (Fig. S10, ESI†).

Furthermore, the obtained  $\text{Co}_2\text{C}$  sample was treated with hydrochloric acid ( $\text{HCl}$ ; 6  $\text{mol L}^{-1}$ ) to exclude the contribution

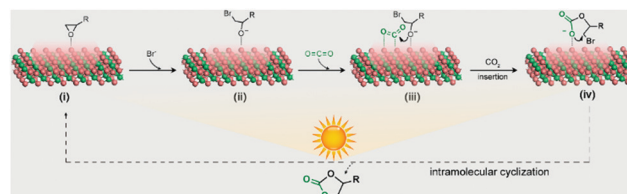
**Table 1** Optimization of the reaction conditions<sup>a</sup>

Entry	Catalyst	Additive	Yield <sup>b</sup> (%)
1	$\text{Co}_2\text{C}$ (0 mg)	TBAB	< 5
2	$\text{Co}_2\text{C}$ (15 mg) <sup>c</sup>	TBAB	54
3	$\text{Co}_2\text{C}$ (15 mg)	TBAB	73.3
4	$\text{Co}_2\text{C}$ (25 mg)	TBAB	93.5
5	$\text{Co}_2\text{C}$ (25 mg) <sup>d</sup>	TBAB	< 5
6	$\text{Co}_2\text{C}$ (25 mg)	—	0
7	$\text{Co}_2\text{C}$ (25 mg) <sup>e</sup>	TBAB	0
8	$\text{Co}_2\text{C}$ (15 mg) <sup>f</sup>	TBAC	26.7
9	$\text{Co}_2\text{C}$ (25 mg) <sup>g</sup>	TBAB	81.9
10	$\text{Co}(\text{OH})_2$ (25 mg)	TBAB	64
11	$\text{CoO}$ (25 mg)	TBAB	63.6
12	$\text{Co}_3\text{O}_4$ (25 mg)	TBAB	48.6
13	$\text{Co}_2\text{C}$ (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  $\text{CH}_3\text{CN}$  as the solvent, blue LEDs ( $\lambda = 450\text{ nm}$ ) as the light source, 15 h. <sup>b</sup> The carbonate product was quantified by  $^1\text{H NMR}$  with diphenylmethanol as the internal standard. The yield was calculated by the equation,  $[\eta (\%) = n(\text{carbonate})/n(3\text{-chloropropylene oxide}) \times 100\%]$ . <sup>c</sup> 0.1 mmol TBAB. <sup>d</sup> No light irradiation. <sup>e</sup>  $\text{N}_2$  instead of  $\text{CO}_2$ . <sup>f</sup> 0.1 mmol TBAC. <sup>g</sup>  $\text{Co}_2\text{C}$  nanoflowers treated with  $\text{HCl}$  (6  $\text{mol L}^{-1}$ ). <sup>h</sup> 0.50 mmol TBAB, AM 1.5 (100  $\text{mW cm}^{-2}$ ) as the light source, 24 h.

of trace amounts of cobalt hydroxide (*i.e.*,  $\text{Co}(\text{OH})_2$ ) and/or cobalt oxide (*i.e.*,  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$ ) on the surface of  $\text{Co}_2\text{C}$  nanoflowers in  $\text{CO}_2$  fixation. After treating the sample with  $\text{HCl}$ , the slightly declined yield of the target product was still much higher than those of pure  $\text{Co}(\text{OH})_2$ ,  $\text{CoO}$ , or  $\text{Co}_3\text{O}_4$  under the same conditions (entries 9–12; Table 1). These results confirmed that  $\text{Co}_2\text{C}$ , but not the hydroxide or oxide impurities, served as the real active sites for  $\text{CO}_2$  fixation. More importantly, the  $\text{Co}_2\text{C}$  catalysed cycloaddition reaction of  $\text{CO}_2$  and epoxides with electron-donating/withdrawing groups could also give rise to products in good to excellent yields ( $\sim 95\%$ ) (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  $\text{Co}_2\text{C}$  nanoflowers catalysed  $\text{CO}_2$ -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  $-0.53\text{ eV}$  (Fig. S12a, see details of density functional theory (DFT) calculations in the ESI†), thereby



**Fig. 3** The proposed mechanism of  $\text{Co}_2\text{C}$  catalysed  $\text{CO}_2$  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.

## Notes and references

- H.-L. Wu, X.-B. Li, C.-H. Tung and L.-Z. Wu, *Adv. Mater.*, 2019, **31**, 1900709.
- X. Jiao, Z. Chen, X. Li, Y. Sun, S. Gao, W. Yan, C. Wang, Q. Zhang, Y. Lin, Y. Luo and Y. Xie, *J. Am. Chem. Soc.*, 2017, **139**, 7586–7594.
- S. C. Peter, *ACS Energy Lett.*, 2018, **3**, 1557–1561.
- J. Ran, M. Jaroniec and S.-Z. Qiao, *Adv. Mater.*, 2018, **30**, 1704649.
- Q. Jiang, Z. Chen, J. Tong, M. Yang, Z. Jiang and C. Li, *Chem. Commun.*, 2017, **53**, 1188–1191.
- S. Wang, B. Y. Guan and X. W. D. Lou, *J. Am. Chem. Soc.*, 2018, **140**, 5037–5040.
- Y. Wang, Z. Zhang, L. Zhang, Z. Luo, J. Shen, H. Lin, J. Long, J. C. S. Wu, X. Fu, X. Wang and C. Li, *J. Am. Chem. Soc.*, 2018, **140**, 14595–14598.
- X. Meng, S. Ouyang, T. Kako, P. Li, Q. Yu, T. Wang and J. Ye, *Chem. Commun.*, 2014, **50**, 11517–11519.
- Q. Guo, F. Liang, X.-B. Li, Y.-J. Gao, M.-Y. Huang, Y. Wang, S.-G. Xia, X.-Y. Gao, Q.-C. Gan, Z.-S. Lin, C.-H. Tung and L.-Z. Wu, *Chem*, 2019, **5**, 2605–2616.
- Y. Bai, J. Zhao, S. Feng, X. Liang and C. Wang, *Chem. Commun.*, 2019, **55**, 4651–4654.
- J. C. Matsubu, V. N. Yang and P. Christopher, *J. Am. Chem. Soc.*, 2015, **137**, 3076–3084.
- D. J. Heldebrant, P. K. Koech, V.-A. Glezakou, R. Rousseau, D. Malhotra and D. C. Cantu, *Chem. Rev.*, 2017, **117**, 9594–9624.
- G. Kuggan, L. J. Abbott, K. E. Hart and C. M. Colina, *Chem. Rev.*, 2018, **118**, 5488–5538.
- X.-B. Li, C.-H. Tung and L.-Z. Wu, *Angew. Chem., Int. Ed.*, 2019, **58**, 10804–10811.
- C. Lu, J. Yang, S. Wei, S. Bi, Y. Xia, M. Chen, Y. Hou, M. Qiu, C. Yuan, Y. Su, F. Zhang, H. Liang and X. Zhuang, *Adv. Funct. Mater.*, 2019, **29**, 1806884.
- F. Liu, K. Huang, Q. Wu and S. Dai, *Adv. Mater.*, 2017, **29**, 1700445.
- M. Ding and H.-L. Jiang, *ACS Catal.*, 2018, **8**, 3194–3201.
- M. Scharfenberg, J. Hilf and H. Frey, *Adv. Funct. Mater.*, 2018, **28**, 1704302.
- T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
- Y. Fan, M. Tiffner, J. Schörgenhuber, R. Robiette, M. Waser and S. R. Kass, *J. Org. Chem.*, 2018, **83**, 9991–10000.
- R. Zevenhoven, S. Eloneva and S. Teir, *Catal. Today*, 2006, **115**, 73–79.
- D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388–2410.
- Y.-X. Zhang, L. Guo, Y.-H. Wang, L.-L. Zhu and Z.-I. Chen, *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.*, 2009, **39**, 445–448.
- X.-B. Lu and D. J. Darensbourg, *Chem. Soc. Rev.*, 2012, **41**, 1462–1484.
- X. Jiang, F. Gou, F. Chen and H. Jing, *Green Chem.*, 2016, **18**, 3567–3576.
- J. Honores, D. Quezada, G. Chacón, O. Martínez-Ferrate and M. J. C. L. Isaacs, *Catal. Lett.*, 2019, **149**, 1825–1832.
- C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin and A. W. Kleij, *J. Am. Chem. Soc.*, 2013, **135**, 1228–1231.
- J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508–3576.
- Q. Yang, C.-C. Yang, C.-H. Lin and H.-L. Jiang, *Angew. Chem., Int. Ed.*, 2019, **58**, 3511–3515.
- H. He, J. A. Perman, G. Zhu and S. Ma, *Small*, 2016, **12**, 6309–6324.
- P.-Z. Li, X.-J. Wang, J. Liu, J. S. Lim, R. Zou and Y. A. Zhao, *J. Am. Chem. Soc.*, 2016, **138**, 2142–2145.
- G. Ji, Z. Yang, H. Zhang, Y. Zhao, B. Yu, Z. Ma and Z. Liu, *Angew. Chem., Int. Ed.*, 2016, **55**, 9685–9689.
- D. Liu, G. Li, J. Liu, Y. Wei and H. Guo, *ACS Appl. Mater. Interfaces*, 2018, **10**, 22119–22129.
- S. Cao, B. Shen, T. Tong, J. Fu and J. Yu, *Adv. Funct. Mater.*, 2018, **28**, 1800136.
- Z. W. Seh, K. D. Fredrickson, B. Anasori, J. Kibsgaard, A. L. Strickler, M. R. Lukatskaya, Y. Gogotsi, T. F. Jaramillo and A. Vojvodic, *ACS Energy Lett.*, 2016, **1**, 589–594.
- R. Zhao, M. Wang, D. Zhao, H. Li, C. Wang and L. Yin, *ACS Energy Lett.*, 2018, **3**, 132–140.
- J. C. Mohandas, M. K. Gnanamani, G. Jacobs, W. Ma, Y. Ji, S. Khalid and B. H. Davis, *ACS Catal.*, 2011, **1**, 1581–1588.
- Q. Guo, F. Liang, X.-Y. Gao, Q.-C. Gan, X.-B. Li, J. Li, Z.-S. Lin, C.-H. Tung and L.-Z. Wu, *ACS Catal.*, 2018, **8**, 5890–5895.
- I. Persson, J. Halim, H. Lind, T. W. Hansen, J. B. Wagner, L. A. Naslund, V. Darakchieva, J. Palisaitis, J. Rosen and P. O. A. Persson, *Adv. Mater.*, 2019, **31**, 1805472.
- J. Wu, Y. Huang, W. Ye and Y. Li, *Adv. Sci.*, 2017, **4**, 1700194.
- J. Peng, X. Chen, W.-J. Ong, X. Zhao and N. Li, *Chem*, 2019, **5**, 18–50.
- L. Zhong, F. Yu, Y. An, Y. Zhao, Y. Sun, Z. Li, T. Lin, Y. Lin, X. Qi, Y. Dai, L. Gu, J. Hu, S. Jin, Q. Shen and H. Wang, *Nature*, 2016, **538**, 84.
- Z. J. Huba and E. E. Carpenter, *CrystEngComm*, 2014, **16**, 8000–8007.
- M. Zamanpour, S. Bennett, P. Taheri, Y. Chen and V. G. Harris, *J. Appl. Phys.*, 2014, **115**, 17A747.
- H. Wang, S. P. Wong, W. Y. Cheung, N. Ke, W. F. Lau, M. F. Chiah and X. X. Zhang, *Mater. Sci. Eng., C*, 2001, **16**, 147–151.
- S. Li, C. Yang, Z. Yin, H. Yang, Y. Chen, L. Lin, M. Li, W. Li, G. Hu and D. Ma, *Nano Res.*, 2017, **10**, 1322–1328.
- D. Gazzoli, M. Occhiuzzi, A. Cimino, D. Cordischi, G. Minelli and F. Pinzari, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 4567–4574.
- L. Yuwen, J. Zhou, Y. Zhang, Q. Zhang, J. Shan, Z. Luo, L. Weng, Z. Teng and L. Wang, *Nanoscale*, 2016, **8**, 2720–2726.