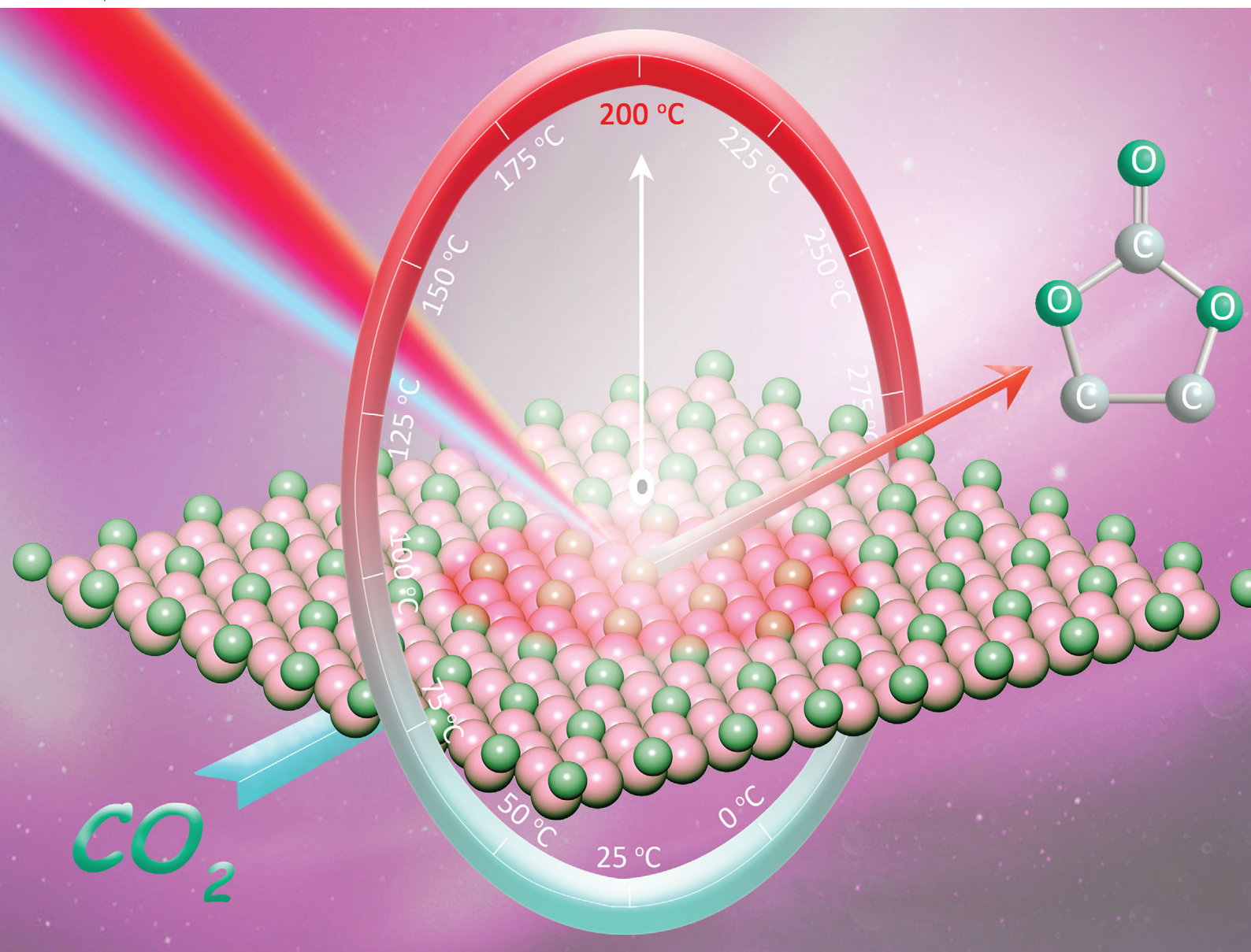


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Flower-like cobalt carbide for efficient carbon dioxide
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Catalytic conversion of carbon dioxide (CO₂) to value-added chemicals under mild conditions is highly desired, albeit with significant challenges. Here, in terms of exposure of abundant active sites and excellent photo-to-thermal conversion properties, flower-like Co₂C has been firstly used for effectively catalysing the cycloaddition of CO₂ 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 CO₂ and epoxide, thus opening up the possibility of a CO₂-epoxide cycloaddition reaction.

The increasing atmospheric concentration of carbon dioxide (CO₂), which is regarded as the main greenhouse gas, has caused serious environmental concerns (*e.g.*, global warming, abnormal climate change and sea level rise).^{1–4} To address the anthropogenic CO₂ emission issues,^{5–11} the approaches of physical CO₂ capture and storage,^{12,13} and chemical conversion of CO₂ into usable fuels and/or value-added chemicals^{14,15} have been widely investigated. From a chemical point of view, cycloaddition of CO₂ with epoxides represents one of the most promising strategies to generate valuable chemicals.^{16–18} By using CO₂ as the renewable and nontoxic one-carbon (C₁) feedstock,¹⁹ cyclic carbonates are produced with 100% atom-economy efficiency.²⁰ Cyclic carbonates can be directly employed in industry as solvents or intermediates, such as carbamates,²¹ polycarbonates²² and spiro compounds.²³ Numerous advances in homogeneous (*e.g.*, Co,^{24,25} Ni,²⁶ Al²⁷ and Cu-based²⁸ monometallic or bimetallic complexes) and heterogeneous (*e.g.*, metal–organic-frameworks (MOFs),^{29–31} mesoporous

polymers,³² and zeolites³³) catalysts have been made for the cycloaddition of CO₂ 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.^{34–36} Cobalt carbide (Co₂C), for example, has been demonstrated to be an effective catalyst in various transformations (*e.g.*, hydrogen evolution and Fischer–Tropsch synthesis).^{37,38} However, the application of cobalt carbide in cycloaddition of CO₂ with epoxides is still elusive. Considering these attributes, we are inspired to explore Co₂C as a novel catalyst for cycloaddition of CO₂ 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 CO₂ and/or epoxides; (ii) the effective CO₂ adsorption ability on TMCs favours the very first step of CO₂ conversion;³⁹ (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^{−1});⁴⁰ and (iv) the feasible separation and reusability of the heterogeneous catalysts is beneficial for large-scale applications.⁴¹ To our delight, flower-like Co₂C facilitates the catalysis of CO₂-epoxide cycloaddition with yields of up to ~95% under visible light (Scheme 1), showing the first example of using TMCs for photothermal-driven CO₂ conversion.

Flower-like Co₂C was synthesized through a modified method of solution pyrolysis at high temperature (Fig. 1a),^{42–44} 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

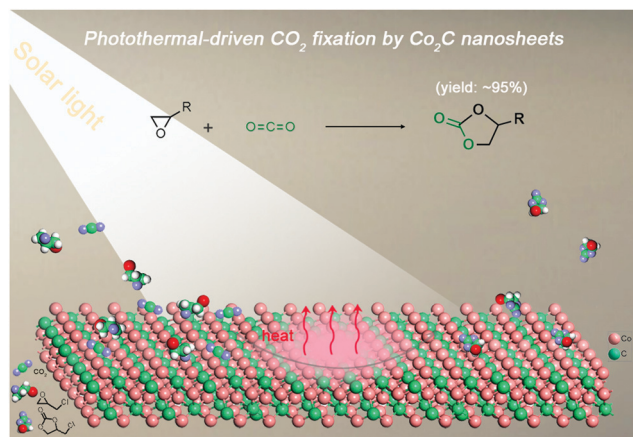
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Scheme 1 Illustration of the photothermal-driven cycloaddition of CO₂ with epoxides catalyzed by Co₂C nanosheets of the nanoflower.

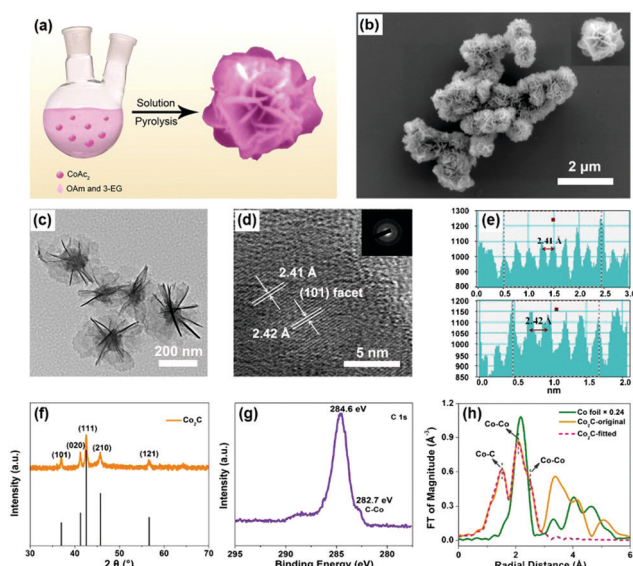


Fig. 1 (a) Synthetic process of flower-like Co₂C. (b) SEM image (the inset panel is the high-resolution SEM image) and (c) TEM image of Co₂C nanoflowers. (d) High-resolution TEM image of Co₂C (the inset panel is the corresponding SAED pattern). (e) The corresponding lattice distances of the exposed (101) plane of Co₂C. (f) XRD pattern and (g) C 1s XPS spectrum of Co₂C nanoflowers. (h) Magnitude of k^2 -weighted Fourier transform of the Co K-edge EXAFS spectra of Co foil and the obtained Co₂C nanoflowers with corresponding curve-fitting results.

individual nanosheets. The thickness of individual nanosheet was determined to be ~ 2.4 nm by atomic force microscopy (AFM) (Fig. S1, ESI[†]). In the high-resolution TEM image, a lattice distance of ~ 2.41 Å was observed, indicating the exposure of the (101) facet of Co₂C (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[†]), 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 Co₂C (Joint Committee on Powder Diffraction Standards (JCPDS) Powder Diffraction File (PDF) No. 65-1457),⁴² indicating the successful formation of Co₂C. The peaks at 1630, 1420 and 1050 cm⁻¹ corresponding to C=C, C-H, and C-N bonds, respectively, in the Fourier transform infrared (FTIR) spectra (Fig. S3, ESI[†]) 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[†]). High-resolution XPS spectra of C 1s (Fig. 1g) and Co 2p (Fig. S5, ESI[†]) show the characteristic peaks of carbide and carbidic Co at 282.7 and 778.1 eV,^{36,45,46} respectively. Combined with the peak at 531.6 eV in the O 1s XPS spectrum (Fig. S6, ESI[†]), the peak at 781.0 eV in the Co 2p XPS spectrum was attributed to the Co(OH)₂ species formed in the process of Co₂C preparation, proving the fact that solution pyrolysis under high temperature inevitably leads to the formation of trace amounts of the hydroxide impurity.^{46,47} 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 Co₂C, see the fitting details in Table S1, ESI[†].

Then, photo-to-thermal conversion effects of Co₂C nanoflowers were experimentally examined. UV-vis-NIR diffuse reflectance spectroscopy (DRS) measurement indicated that the synthesized Co₂C nanoflowers showed strong absorption in the range of 300 to 1200 nm (Fig. S7, ESI[†]), directly confirming its excellent light-harvesting properties. When the water suspension of Co₂C nanoflowers (0.6 mg mL⁻¹) was exposed to a 635 nm laser at varied power densities (0.1, 0.5, 1.0 and 2.0 W cm⁻²), the solution displayed apparent temperature elevation (Fig. 2a). For instance, under 635 nm laser irradiation (0.5 W cm⁻²), the temperature of the Co₂C 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[†]). Huge amount of heat released from Co₂C 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 Co₂C sample quickly increased to 116.8 °C upon exposure to a 635 nm laser (0.5 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 (η), regarded as a major parameter in evaluating the performance in converting light to heat of a given material,⁴⁸ of the flower-like Co₂C was calculated to be as high as $\sim 63.1\%$ at 635 nm (Fig. 2b and c, see details in the ESI[†]). The exceptional photo-to-thermal conversion performance of Co₂C nanoflowers obtained here was comparable with those of the reported materials (Table S2, ESI[†]). To further evaluate its photothermal stability, temperature variations of Co₂C nanoflowers suspension were recorded under light irradiation (laser on) followed by natural cooling to room temperature (laser off). As shown in Fig. 2d,

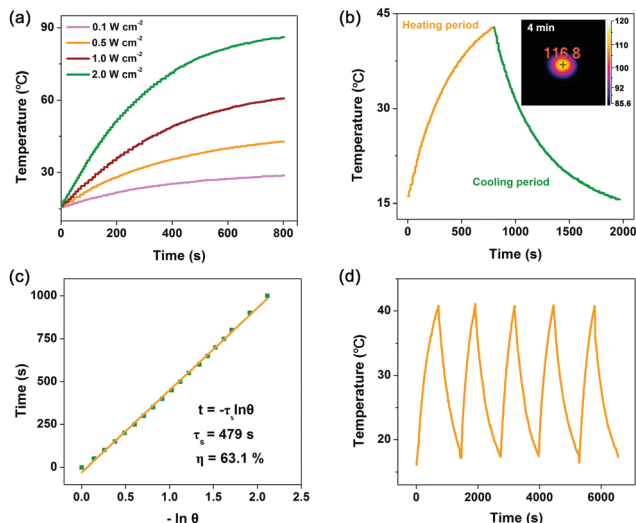


Fig. 2 (a) Photothermal heating curves of Co_2C nanoflowers dispersed in water under 635 nm laser irradiation at varied power densities (0.1, 0.5, 1.0 and 2.0 W cm^{-2}). (b) Photothermal effect of Co_2C aqueous dispersion under 635 nm laser irradiation (0.5 W cm^{-2}) and the cooling process after laser off. The inset panel in (b) is the IR image of Co_2C powder under 635 nm laser irradiation (0.5 W cm^{-2}) for 4.0 min. (c) The corresponding time constant (τ_s) for the heat transfer from the system determined by applying the linear time data from cooling period. (d) Recycling-heating curves of the Co_2C aqueous suspension with 635 nm laser irradiation at 0.5 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 Co_2C nanoflowers as durable photothermal materials.

To investigate the catalytic performance of Co_2C 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_2C 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 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 Br^- compared to Cl^- dramatically benefited the ring-opening reaction of epoxides.²⁹ To verify the photothermal effects of Co_2C 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°C), implying that the photothermal effects could promote the cycloaddition reaction between CO_2 and epoxide (Fig. S10, ESI†).

Furthermore, the obtained Co_2C sample was treated with hydrochloric acid (HCl ; 6 mol L^{-1}) to exclude the contribution

Table 1 Optimization of the reaction conditions^a

Entry	Catalyst	Additive	Yield ^b (%)
1	Co_2C (0 mg)	TBAB	< 5
2	Co_2C (15 mg) ^c	TBAB	54
3	Co_2C (15 mg)	TBAB	73.3
4	Co_2C (25 mg)	TBAB	93.5
5	Co_2C (25 mg) ^d	TBAB	< 5
6	Co_2C (25 mg)	—	0
7	Co_2C (25 mg) ^e	TBAB	0
8	Co_2C (15 mg) ^f	TBAC	26.7
9	Co_2C (25 mg) ^g	TBAB	81.9
10	$\text{Co}(\text{OH})_2$ (25 mg)	TBAB	64
11	CoO (25 mg)	TBAB	63.6
12	Co_3O_4 (25 mg)	TBAB	48.6
13	Co_2C (50 mg) ^h	TBAB	66.4

^a Reaction conditions: 0.15 mmol 3-chloropropylene oxide, 0.25 mmol TBAB, 3 mL CH_3CN as the solvent, blue LEDs ($\lambda = 450\text{ nm}$) as the light source, 15 h. ^b The carbonate product was quantified by $^1\text{H NMR}$ with diphenylmethanol as the internal standard. The yield was calculated by the equation, $[\eta (\%) = n(\text{carbonate})/n(3\text{-chloropropylene oxide}) \times 100\%]$. ^c 0.1 mmol TBAB. ^d No light irradiation. ^e N_2 instead of CO_2 . ^f 0.1 mmol TBAC. ^g Co_2C nanoflowers treated with HCl (6 mol L^{-1}). ^h 0.50 mmol TBAB, AM 1.5 (100 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.*, CoO and Co_3O_4) on the surface of Co_2C nanoflowers in CO_2 fixation. After treating the sample with HCl , the slightly declined yield of the target product was still much higher than those of pure $\text{Co}(\text{OH})_2$, CoO , or Co_3O_4 under the same conditions (entries 9–12; Table 1). These results confirmed that Co_2C , but not the hydroxide or oxide impurities, served as the real active sites for CO_2 fixation. More importantly, the Co_2C catalysed cycloaddition reaction of 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 Co_2C nanoflowers catalysed 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 eV (Fig. S12a, see details of density functional theory (DFT) calculations in the ESI†), thereby

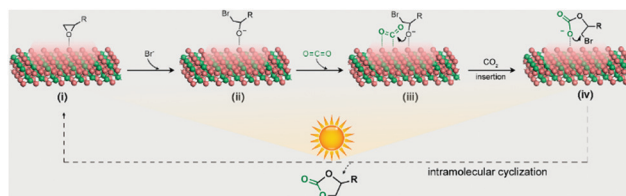


Fig. 3 The proposed mechanism of Co_2C catalysed CO_2 cycloaddition with epoxides under light irradiation.

leading to the elongation of C–O bond from 1.956 to 2.086 Å. Then, the nucleophilic Br[−] 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, CO₂ 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 Co₂C nanoflowers, the oxygen anion of the alkoxide intermediate combines with the adjacent highly activated CO₂ 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 Co₂C, the endothermic CO₂ cycloaddition reaction proceeds with high yields, which is comparable with the reported results (Table S4, ESI†).

In summary, an efficient CO₂ cycloaddition reaction with epoxides is achieved on low-priced photothermal catalyst of Co₂C nanoflowers. The yield of cyclic carbonates is up to ~95% with visible-light irradiation, owing to the excellent photothermal effects of Co₂C nanoflowers in converting light to heat. Besides, the high specific area as well as efficient CO₂ adsorption on the exposed Co atoms of the catalysts can simultaneously activate the adsorbed CO₂ and epoxides, thus promoting the CO₂ 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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