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As a unique class of functional materials, perovskite oxides have shown great opportunities in various energy storage and conversion applications. However, their performance for boosting photocatalytic CO<sub>2</sub> reduction is seldom reported. Herein, we report the facile synthesis of coralline-like LaCoO<sub>3</sub> perovskite materials and their use as highly efficient and stable cocatalysts for splitting CO<sub>2</sub> into CO with visible light.

The generation of valuable chemicals/fuels using the greenhouse gas CO2 as carbon source has long been regarded as a perfect solution to address the problems of global warming and energy shortage.<sup>1</sup> Semiconductor-mediated photocatalytic reduction of CO<sub>2</sub> with abundant solar energy as the energy input is thus attracting considerable attention.<sup>2</sup> However, efficient and stable CO<sub>2</sub> photoreduction by man-made materials is a very challenging task, due to the chemically inert characteristic of linear CO<sub>2</sub> molecules and the high recombination rate of photogenerated charge carriers during phtocatalysis.<sup>3</sup> Although enormous research efforts have been made to construct hybrid chemical systems to operate CO<sub>2</sub> reduction photocatalysis, further improvements of the quantum efficiency is still highly necessary to meet the requirements of practical utilization.

To establish photocatalytic CO<sub>2</sub> conversion systems with high efficiency and selectivity, the employment of cocatalyst is of vital importance because of their multifunction for promoting the transfer kinetics of photoinduced charges, modulating the distribution of reaction products, and lowering the activation energy for CO<sub>2</sub> conversion reactions.<sup>4</sup> Comparing with the commonly used noble metal cocatalysts (e.g., Pt, Au, Ag, Pd),<sup>5</sup> the exploitation of new cocatalysts made of earth abundant elements is more attractive from the viewpoint of large-scale commercialization.<sup>6</sup>

Recently, perovskite oxides (ABO<sub>3</sub>), a unique type of functional materials, have aroused significant research interests in energy storage and conversion areas, due mainly to their stable crystal structure, excellent electromagnetic properties, and high catalytic activities for target reactions.<sup>7</sup> The strong hybridization between the O2p and the transition-metal 3d orbitals in the BO<sub>6</sub> octahedra could induce structural distortions and/or B site valence transformations, thus modifying their physiochemical properties for enhanced catalysis performance.<sup>8</sup> Thereinto, the lanthanum-based perovskite oxide (LaCoO<sub>3</sub>) has shown prodigious vitality as active catalysts for reduction reactions,9 and elements doping is considered as an efficient way to further improve the performance of this material.<sup>10</sup> However, the use of LaCoO<sub>3</sub> as a cocatalyst cooperative with a photosensitizer to realize efficient CO2 photoreduction has never been reported.



Fig. 1 (a) XRD pattern and (b) crystal structure of perovskite LaCoO<sub>3</sub>.

Herein, we demonstrate the synthesis of coralline-like LaCoO<sub>3</sub> and its application as a highly active cocatalyst for improving photochemical reduction of CO<sub>2</sub> under visible light irradiation. The LaCoO<sub>3</sub> material was synthesized by a citrate gel method and a subsequent thermal treatment in air. The powder X-ray diffraction (XRD) characterization was first conducted to investigate

### Perovskite oxide LaCoO<sub>3</sub> cocatalyst for efficient

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## photocatalytic reduction of CO<sub>2</sub> with visible light

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the crystallographic structure and the phase purity of the prepared  $LaCoO_3$  sample. As shown in Fig. 1a, all the diffraction peaks in the XRD pattern of  $LaCoO_3$  sample can be well identified as rhombohedral phase (JCPDS file No. 48-0123) with lattice constants a=5.44 Å, b=5.44 Å, c=13.09 Å. No any other characteristic peaks are observed, indicting high phase purity of the obtained  $LaCoO_3$  material. The crystal structure of perovskite  $LaCoO_3$  is illustrated in Fig. 1b, where the lanthanum ions are dispersed in the centre of the cobalt oxide octahedron as.



Fig. 2 (a, b) SEM images, (c) TEM image, and (d) EDX pattern of the as-prepared LaCoO<sub>3</sub> sample. Insert in (c) is the corresponding high resolution TEM image.

The morphological structure of the perovskite LaCoO<sub>3</sub> material was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. 2a, the typical low-magnification SEM image reveals nanosized spherical particles interconnected firmly with each other, constructing highly porous layered fragments. In the high-magnification SEM image (Fig. 2b), the spherical nanoparticles can be clearly observed with the sizes range from 50 to 200 nm. TEM image confirms the sheetlike mesoporous structure of the LaCoO<sub>3</sub> sample (Fig. 2c). The visible lattice fringes in the high resolution TEM (HRTEM) image are readily indexed to the interplanar spacing of a rhombohedral LaCoO<sub>3</sub> structure. Energy dispersive X-ray (EDX) measurement was conducted to determine the elemental composition of the LaCoO<sub>3</sub> sample. As shown in Fig. 2d, only single peaks of La, Co and O elements are observed with the corresponding La/Co atomic ratio of ca. 1:1, which further validates the purity of the synthesized perovskite material.

Elemental composition and detailed oxidation state of the elements of the LaCoO<sub>3</sub> sample were investigated by the X-ray photoelectron spectroscopy (XPS) characterization. The survey spectrum only displays the signal peaks of La, Co, and O elements, consistent with the results of EDX characterization (Fig. S1a, ESI<sup>†</sup>). In the Co 2p high resolution XPS spectrum, two peaks positioned at 794.8 and 780.0 eV are observed, corresponding to Co  $2p_{1/2}$  and Co  $2p_{3/2}$ , respectively (Fig. S1b, ESI<sup>†</sup>). The binding energy of the peaks detected for Co 2p matches well with that of other ternary cobalt

oxides, which indicates Co(III) is the main oxidation state.<sup>11</sup> The high resolution XPS spectrum of La 3d presents two regions, among which the peaks with binding energy of 851.5 and 834.8 eV are correspondingly assigned to La  $3d_{3/2}$  and La  $3d_{5/2}$ , and the rest two peaks located at 855.0 and 838.0 eV are attributed to the corresponding shake-up peaks (Fig. S1c, ESI<sup>†</sup>), suggesting La holds chemical valance of +3 in the LaCoO<sub>3</sub> sample.<sup>12</sup> The O 1s high resolution XPS spectrum can be well fitted into two peaks located at 528.8 and 531.2 eV, ascribing to the crystal lattice oxygen and surface hydroxyl, respectively (Fig. S1d, ESI<sup>†</sup>).<sup>13</sup>

 $N_2$  adsorption-desorption measurements were carried out to study texture properties of the LaCoO<sub>3</sub> sample. Results reveal that the  $N_2$  adsorption-desorption isotherms can be categorized as type IV with a type H1 hysteresis loop (Fig. S2a, ESI<sup>†</sup>), pointing to its mesoporous characteristics. The BET surface area is measured to be *ca.* 12 m<sup>2</sup> g<sup>-1</sup>. Besides, to further demonstrate the opportunity of LaCoO<sub>3</sub> sample for CO<sub>2</sub> photoreduction, CO<sub>2</sub> adsorption measurement was conducted. As shown in Fig. S2b (ESI<sup>†</sup>), this porous LaCoO<sub>3</sub> material shows a maximum CO<sub>2</sub> uptake of 15 cm<sup>3</sup> g<sup>-1</sup>, which may promise the LaCoO<sub>3</sub> solid with high activity for CO<sub>2</sub> reduction catalysis.



 $\tilde{E}_{0}$   $\tilde{E}_{1}$   $\tilde{E}_{1}$   $\tilde{E}_{2}$   $\tilde{E}_{2}$ 

The LaCoO<sub>3</sub> catalysed CO<sub>2</sub> reduction reaction was performed in a CO<sub>2</sub>-saturated MeCN/H<sub>2</sub>O mixture under visible light irradiation with a Ru-complex (abbreviated as **Ru**) and triethanolamine (TEOA) as the photosensitizer and electron donor, respectively. As shown in Fig. 3a, after reaction for 30 min under normal conditions, 28.5 µmol CO and 9.1 µmol H<sub>2</sub> were detected as the main products, corresponding to a high CO selectivity of 76% and an apparent quantum yield (AQY) of 1.36%. The production of CO is about 20 times higher than that of LaCoO<sub>3</sub>-free system under otherwise the same conditions. These observations underline the high catalytic activity of LaCoO<sub>3</sub> cocatalyst for facilitating the CO<sub>2</sub>-to-CO conversion reaction in the developed photochemical system. Control experiments revealed that if visible light or the **Ru**  photosensitizer was removed from the reaction system, the  $CO_2$  reduction catalysis was completely stopped, indicating the  $CO_2$  reduction reaction is started by visible light excitation of the photosensitizer. When the reaction was conducted in Ar atmosphere, no any CO was detected, suggesting that the formed CO was originated from the gas source of  $CO_2$ . The carbon origin of CO was further explored by <sup>13</sup>C-labelled isotropic experiment. Results of GC-MS analysis for the produced gases present a peak at 4.2 min with the corresponding *m*/*z* value of 29, which is assigned to <sup>13</sup>CO (Fig. S3, ESI†). This result straightforwardly validates that  $CO_2$  is the carbon source of the generated CO.

The time course for the evolution of CO and  $H_2$  is depicted in Fig. 3b. As can be seen, the yield of CO and  $H_2$  increased markedly during the initial photoreaction for about 1 hour, and thereafter the generation rate of the products diminished gradually. This is a common phenomenon in metal-complex-sensitized photochemical CO<sub>2</sub> reduction systems, which is mainly caused by the exhaustion of dye photosensitizer after long time operations.<sup>14</sup> Stability of LaCoO<sub>3</sub> cocatalyst was studied by the cycling experiments. Results show that no distinct decrease in CO/H<sub>2</sub> evolution is observed after repeated reaction for 6 cycles (Fig. 3c), indicating the good reusability of the perovskite cocatalyst in the CO<sub>2</sub> photoreduction system.

After photocatalytic reaction, the LaCoO<sub>3</sub> solid was separated from the reaction mixture. Results of ICP-MS measurements for the resultant supernatant confirm that only less than 0.3% cobalt ions were detected, which indicates that negligible cobalt ions falling off from the perovskite materials. Meanwhile, the used LaCoO<sub>3</sub> sample was further characterized by XRD and XPS. As shown in Fig. S4 (ESI<sup>†</sup>), no noticeable difference in the XRD patterns and XPS spectra were observed between the fresh and used LaCoO<sub>3</sub> samples. All these findings firmly evidence the structural stability of the LaCoO<sub>3</sub> cocatalyst in current CO<sub>2</sub> reduction system.

The  $CO_2$  reduction photocatalysis was also investigated under photoirradiation with different wavelength. As shown in Fig 3d, the trend of CO/H<sub>2</sub> yield matches well with the optical absorption spectrum of the **Ru** photosensitizer. This observation reveals that the CO<sub>2</sub>-to-CO conversion reaction proceeds photocatalytically by light excitation of the **Ru** complex as a solar energy transducer for tandem redox reactions.

To highlight the superior function of perovsikte LaCoO<sub>3</sub> for promoting the CO<sub>2</sub> conversion catalysis, its catalytic performance was further compared with some typical cobaltcontaining ternary oxides under similar conditions.<sup>15</sup> As listed in Table S1 (ESI<sup>†</sup>), the CO<sub>2</sub> reduction efficiency of the perovskite material is almost two times higher than that of other spinel cobalt oxides. These data is a strong indication that the LaCoO<sub>3</sub> material is excellent heterogeneous cocatalyst capable of facilitating CO<sub>2</sub> reduction photocatalysis by merging the synergistic functions of catalytically active Co and La species confined in the crystal structure of perovskite with the merits of coralline-like porous nanoarchitectures.

The flat-band potential of the  $LaCoO_3$  sample was determined by Mott-Schottky plot. Results show that the conduction band level of

LaCoO<sub>3</sub> is *ca.* -0.63 V (*vs.* NHE, pH = 7.0) (Fig. S5, ESI<sup>†</sup>), which is lower than the redox potential of  $E(Ru^{2+}/Ru^{3+}) = -0.86$  V (*vs.* NHE, pH = 7.0) and higher than that of  $E(CO_2/CO) = -0.53$  V (*vs.* NHE, pH = 7.0),<sup>16</sup> ensuring the feasibility of photoexcited electrons transferring from **Ru** photosensitizer to LaCoO<sub>3</sub> cocatalyst to split CO<sub>2</sub> into CO.<sup>15, 17</sup>

In conclusion, coralline-like LaCoO<sub>3</sub> perovskite material has been synthesized by a facile citrate gel method coupled with a thermal treatment in air. For the first time, the prepared LaCoO<sub>3</sub> material was proved to be a highly efficient and stable cocatalyst for reducing CO<sub>2</sub> to CO under visible-light irradiation. This work demonstrates the first but very important application of perovskite materials for supporting photocatalytic reduction of CO<sub>2</sub> cooperative with a metalcomplex light harvester. Moreover, this work also promises the great opportunities of perovskite/semiconductor composites for developing advanced CO<sub>2</sub> reduction systems made of earth abundant materials.

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#### Notes and references

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- (a) R. Kuriki, H. Matsunaga, T. Nakashima, K. Wada, A. Yamakata, O. Ishitani and K. Maeda, *J. Am. Chem. Soc.*, 2016, **138**, 5159. (b)
   S. Wang and X. Wang, *Angew. Chem. Int. Ed.*, 2016, **55**, 2308. (c)
   T. Jin, C. Liu and G. Li, *Chem. Comm.*, 2014, **50**, 6221. (d) C. K. Rofer-DePoorter, *Chem. Rev.*, 1981, **81**, 447
- 2 (a) J. Qin, S. Wang, H. Ren, Y. Hou and X. Wang, *Appl. Catal., B*, 2015, **179**, 1. (b) S. Wang, X. Wang, *Small*, 2015, **11**, 3097. (c) K. Maeda, K. Sekizawa and O. Ishitani, *Chem. Comm.*, 2013, **49**, 10127. (d) J. Lin, Z. Pan and X. Wang, *ACS Sustainable Chem. & Eng.*, 2014, **2**, 353. (e) B. Pan, Y. Zhou, W. Su and X. Wang, *Nano Res.*, 2017, **10**, 534. (f) Q. Liu, Y. Zhou, J. Kou, X. Chen, Z. Tian, J. Gao, S. Yan and Z. Zou, *J. Am. Chem. Soc.*, 2010, **132**, 14385; (g) S. Wang, B. Y. Guan, Y. Lu and X. W. Lou, *J. Am. Chem. Soc.*, **2017**, *139*, 17305.
- (a) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365.
   (b) S. N. Habisreutinger, L. Schmidt-Mende and J. K. Stolarczyk, *Angew. Chem. Int. Ed.*, 2013, **52**, 7372.
   (c) S. Wang and X. Wang, *Appl. Catal.*, *B*, 2015, **162**, 494.
   (d) M. Li, L. Zhang, X. Fan, Y. Zhou, M. Wu and J. Shi, *J. Mater. Chem. A*, 2015, **3**, 5189.
- 4 (a) J. Qin, S. Wang and X. Wang, *Appl. Catal., B,* 2017, 209, 476.
  (b) K. Zhao, J. Qi, S. Zhao, H. Tang, H. Yin, L. Zong, L. Chang, Y. Gao, R. Yu and Z. Tang, *Chin. J. Catal.*, 2015, 36, 261. (c) B. Pan, Y. Zhou, W. Su and X. Wang, *RSC Adv.*, 2016, 6, 34744. (d) J.-M.

Published on 05 February 2018. Downloaded by University of Reading on 06/02/2018 02:17:05

Lehn, R. Ziessel, *Proc. Natl. Acad. of Sci. U.S.A.*, 1982, **79**, 701-704. (e) A. J. Morris, G. J. Meyer and E. Fujita, *Acc. Chem. Res.*, 2009, **42**, 1983.

- 5 (a) S. Posada-Pérez, P. J. Ramírez, J. Evans, F. Viñes, P. Liu, F. Illas and J. A. Rodriguez, *J. Am. Chem. Soc.*, 2016, 138, 8269. (b) Z. Zhu, J. Qin, M. Jiang, Z. Ding and Y. Hou, *Appl. Surf. Sci.*, 2017, 391, 572. (c) P. Kar, S. Farsinezhad, N. Mahdi, Y. Zhang, U. Obuekwe, H. Sharma, J. Shen, N. Semagina and K. Shankar, *Nano Res.*, 2016, 9, 3478. (d) B. Pan, S. Luo, W. Su and X. Wang, *Appl. Catal., B*, 2015, 168–169, 458. (e) G. Gao, Y. Jiao, E. R. Waclawik and A. Du, *J. Am. Chem. Soc.*, 2016, 138, 6292. (f) S. Xie, Y. Wang, Q. Zhang, W. Deng and Y. Wang, *ACS Catal.*, 2014, 4, 3644. (g) Q. Wang, P. Dong, Z. Huang and X. Zhang, *Chem. Phys. Lett.*, 2015, 639, 11.
- 6 (a) S. Wang, J. Lin and X. Wang, *Phys. Chem. Chem. Phys.*, 2014, 16, 14656. (b) C. Gao, Q. Meng, K. Zhao, H. Yin, D. Wang, J. Guo, S. Zhao, L. Chang, M. He, Q. Li, H. Zhao, X. Huang, Y. Gao and Z. Tang, *Adv. Mater.*, 2016, 28, 6485. (c) S. Wang, B. Guan and X. Lou, *Energy Environ. Sci.*, 2018, DOI: 10.1039/C7EE02934A.
- 7 (a) M. Gibert, P. Zubko, R. Scherwitzl, J. Íñiguez and J.-M. Triscone, *Nat. mater.*, 2012, **11**, 195. (b) J. R. Petrie, V. R. Cooper, J. W. Freeland, T. L. Meyer, Z. Zhang, D. A. Lutterman and H. N. Lee, *J. Am. Chem. Soc.*, 2016, **138**, 2488. (c) K. Iizuka, T. Wato, Y. Miseki, K. Saito and A. Kudo, *J. Am. Chem. Soc.*, 2011, **133**, 20863. (d) W. Wang, M. O. Tadé and Z. Shao, *Chem. Soc. Rev.*, 2015, **44**, 5371.
- 8 (a) J. Zhang, D. Tan, Q. Meng, X. Weng and Z. Wu, *Appl. Catal., B*, 2015, **172**, 18. (b) P. Ravindran, P. Korzhavyi, H. Fjellvåg and A. Kjekshus, *Phys. Rev. B*, 1999, **60**, 16423. (c) E. Campagnoli, A. Tavares, L. Fabbrini, I. Rossetti, Y. A. Dubitsky, A. Zaopo and L. Forni, *Appl. Catal., B*, 2005, **55**, 133.
- 9 (a) J. Sunarso, A. A. J. Torriero, W. Zhou, P. C. Howlett and M. Forsyth, J. Phys. Chem. C, 2012, 116, 5827. (b) D. Meziani, A. Reziga, G. Rekhila, B. Bellal and M. Trari, Energy Convers. Manage., 2014, 82, 244.
- 10 L. Jia, J. Li and W. Fang, Catal. Commun., 2009, 11, 87.
- (a) D. Barreca, C. Massignan, S. Daolio, M. Fabrizio, C. Piccirillo, L. Armelao and E. Tondello, *Chem. Mater.*, 2001, **13**, 588. (b) D. G. Castner, P. R. Watson and I. Y. Chan, *J. Phys. Chem.*, 1989, **93**, 3188. (c) J. Bai, X. Li, G. Liu, Y. Qian, S. Xiong, *Adv. Funct. Mater.*, 2014, **24**, 3012. (d) W. Wei, W. Chen, D. G. Ivey, *Chem. Mater.*, 2008, **20**, 1941.
- 12 (a) B. Pan, Q. Xie, H. Wang, J. Zhu, Y. Zhang, W. Su and X. Wang, *J. Mater. Chem. A*, 2013, **1**, 6629. (b) R. R. Solís, F. J. Rivas, O. Gimeno and J.-L. Pérez-Bote, *J. Chem. Technol. Biotechnol.*, 2017, DOI: 10.1002/jctb.5228.
- 13 (a) T. F. Huang, S. G. Mohamed, C. C. Shen, Y. Q. Tsai, W. S. Chang, R. S. Liu, *Nanoscale*, 2013, **5**, 12115. (b) J. P. Dacquin, C. Lancelot, C. Dujardin, P. Da Costa, G. Djega-Mariadassou, P. Beaunier, S. Kaliaguine, S. Vaudreuil, S. Royer and P. Granger, *Appl. Catal., B*, 2009, **91**, 596. (c) S. Kaliaguine, A. Van Neste, V. Szabo, J. E. Gallot, M. Bassir and R. Muzychuk, *Appl. Catal., A*, 2001, **209**, 345.
- 14 (a) R. Ziessel, J. Hawecker and J.-M. Lehn, *Helv. Chim. Acta*, 1986, 69, 1065. (b) S. Wang, W. Yao, J. Lin, Z. Ding, X. Wang, *Angew. Chem. Int. Ed.*, 2014, 53, 1034. (c) J. M. Lehn, R. Ziessel, *J.*

*Organomet. Chem.*1990, **382**, 157. (d) M. Jiang, Y. Gao, Z. Wang and Z. Ding, *Appl. Catal.*, *B*, 2016, **198**, 180.

- 15 (a) Z. Wang, M. Jiang, J. Qin, H. Zhou and Z. Ding, *Phys. Chem. Chem. Phys.*, 2015, **17**, 16040. (b) S. Wang, Y. Hou and X. Wang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 4327. (c) S. Wang, Z. Ding and X. Wang, *Chem. Commun.*, 2015, **51**, 1517.
- 16 (a) K. Kalyanasundaram, Coord. Chem. Rev., 1982, 46, 159. (b) J. Schneider, H. Jia, J. T. Muckerman and E. Fujita, *Chem. Soc. Rev.*, 2012, **41**, 2036.
- (a) X. Lin, Y. Gao, M. Jiang, Y. Zhang, Y. Hou, W. Dai, S. Wang, Z. Ding, *Appl. Catal. B: Environ.*, 2018, 224, 1009. (b) Y. Gao, L. Ye, S. Cao, H. Chen, Y. Yao, J. Jiang and L. Sun, *ACS Sustainable Chem. Eng.*, DOI: 10.1021/acssuschemeng.7b03119.

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#### **TOC Figure**

