



Supporting Information

for *Small*, DOI: 10.1002/smll.202007025

CO₂ Footprint of Thermal Versus Photothermal CO₂
Catalysis

*Shenghua Wang, Athanasios A. Tountas, Wangbo Pan,
Jianjiang Zhao, Le He, Wei Sun, Deren Yang,* and
Geoffrey A. Ozin**

Supporting Information

CO₂ Footprint of Thermal versus Photothermal CO₂ Catalysis

Shenghua Wang, Athanasios A. Tountas, Wangbo Pan, Jianjiang Zhao, Le He, Wei Sun*, Deren Yang*, and Geoffrey A. Ozin*

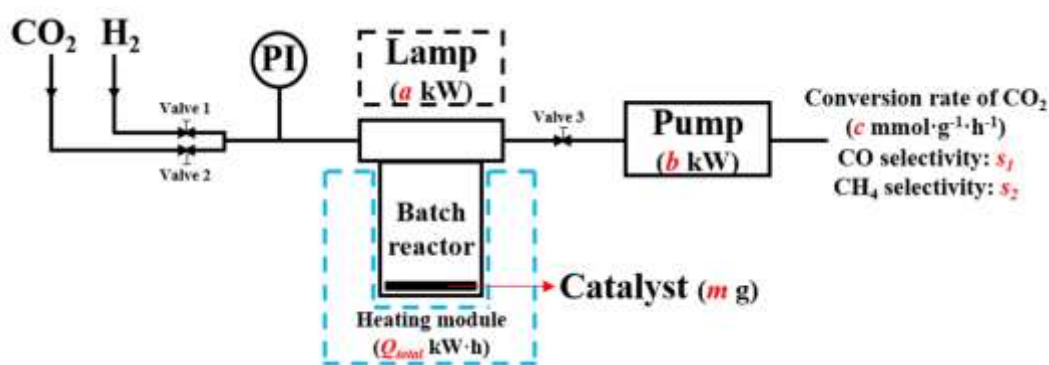


Figure S1. The major components, auxiliary equipment, and key parameters for a typical batch reactor.

In a typical cycle for the batch reactor, valve 1 and valve 2 are closed while valve 3 is open at the beginning. A pump is used to evacuate the reactor within t_2 hours, after which, valve 3 will be closed. Valve 1 and valve 2 will then be open to feed the reactor with fresh reactants within t_3 hours. Next, valve 1 and valve 2 will be closed to keep the gaseous reactants in a closed system. A lamp or a heating module will be utilized to drive the reaction within t_1 hours.

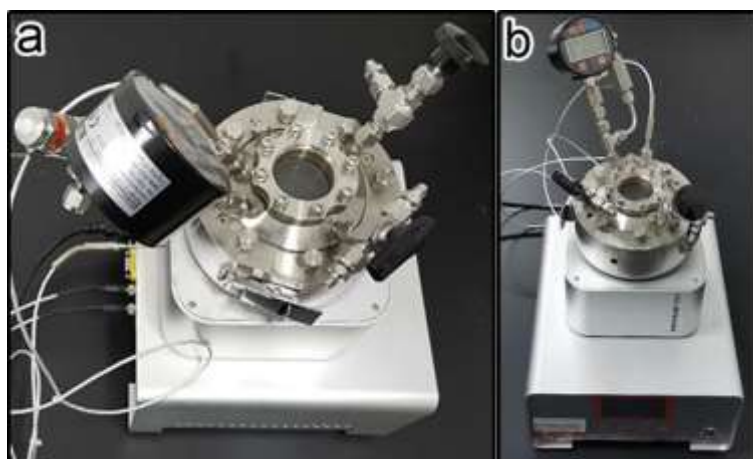


Figure S2. The digital photos of the batch reactor in our laboratory, which allows both light and heat input.

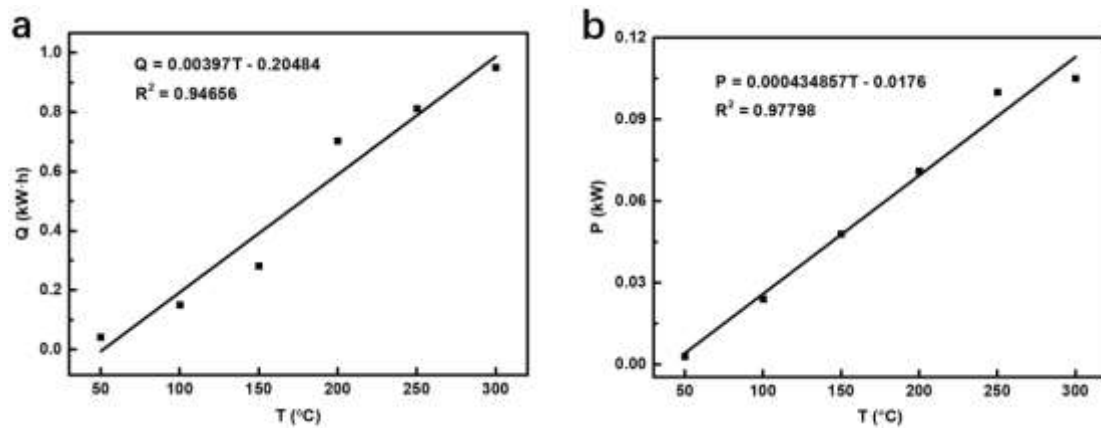


Figure S3. The power consumed in the (a) initial heating process and (b) the equilibrium region of maintaining the target temperature for our batch reactor.

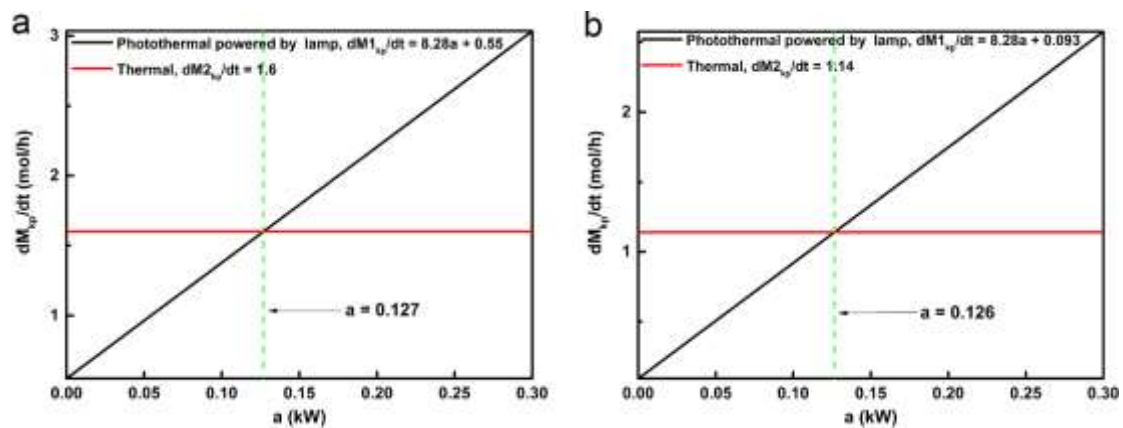


Figure S4. The dependence of net CO₂ reduction rate on the power of lamp when a single pump supports (a) one batch reactor and (b) six batch reactors. The dashed lines mark the threshold below which the photothermal process driven by lamp has a lower CO₂ footprint than them thermal process.

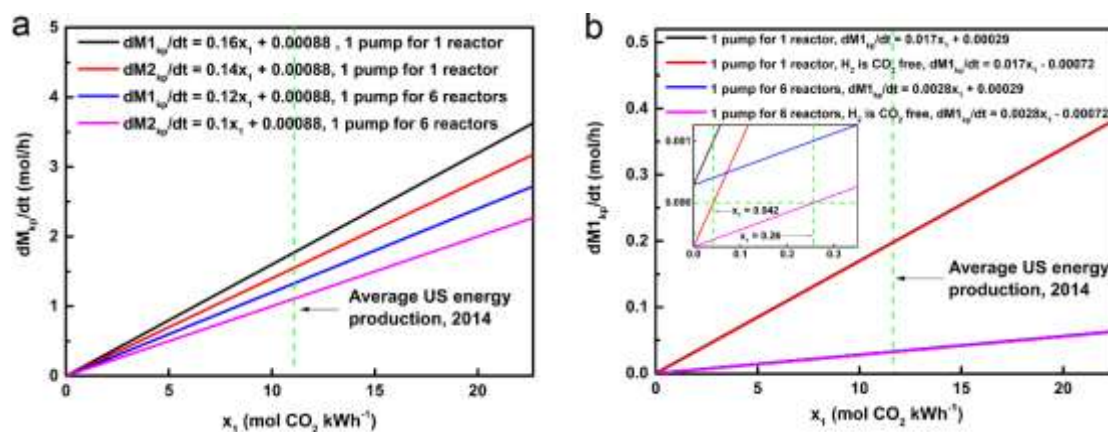


Figure S5. The dependence of net CO₂ reduction rate on CO₂ emission per kWh of electricity (x_1) for batch reactors when (a) 150 W lamp and (b) sunlight are used as the illumination source, respectively. The plots for thermocatalysis ($dM2_{kp}/dt$) are also shown for reference. The inset in (b) shows the maximum x_1 which can achieve net CO₂ reduction.

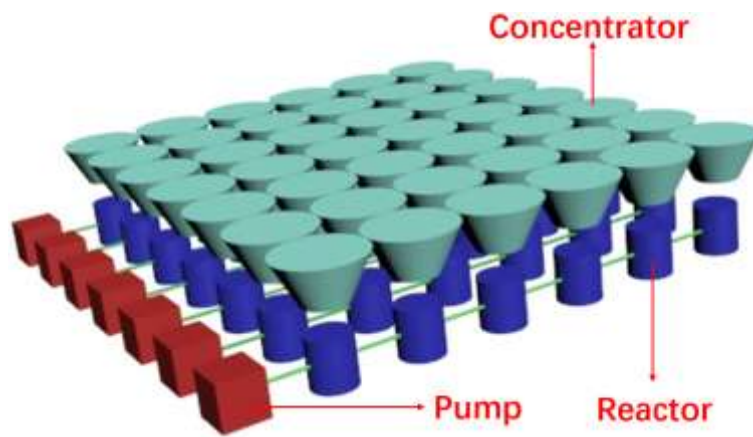


Figure S6. Blueprint of the scheme for a green house filled with batch reactors.

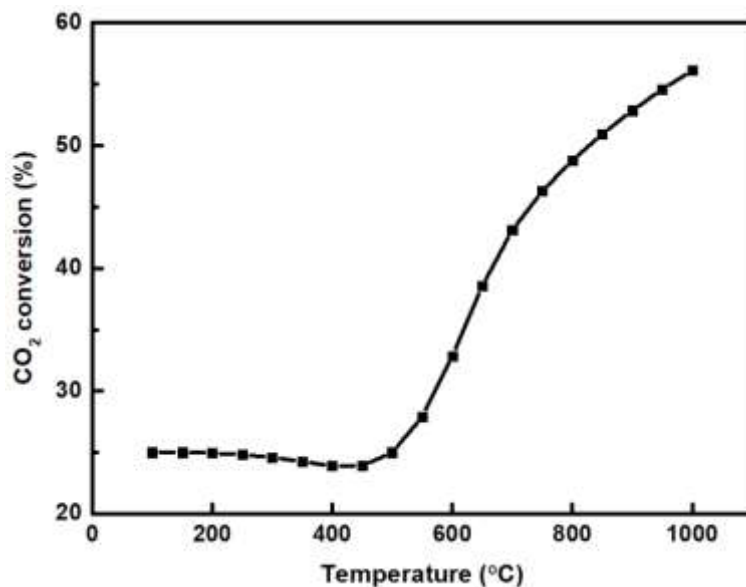


Figure S7. The ideal conversion rate of CO₂ under different temperatures for batch reactors calculated from Aspen. CO₂: H₂ = 1:1, pressure = 105.5 kPag (15.3 Psig), and both RWGS and Sabatier reactions have been considered. An ideal c value of 0.4 mol g⁻¹ h⁻¹ can be derived using the reaction parameters reported in the paper of Wang *et al.* (Table S1).

According to the derived data from the paper of Wang *et al.* used in our analysis, the feed amount of CO₂ (n_{CO_2}) in a cycle is 0.0042 mol, the irradiation time in a cycle (t_I) is 0.5 hours, and the mass of the catalyst (m) is 0.12 g. The maximum value of CO₂ conversion efficiency (η_{max}) in Fig. S7 is taken as 0.56 at 1000°C. Therefore, the ideal value of c should equal $(n_{CO_2} * \eta_{max}) / (m * t_I) = 0.04$ mol g⁻¹ h⁻¹.

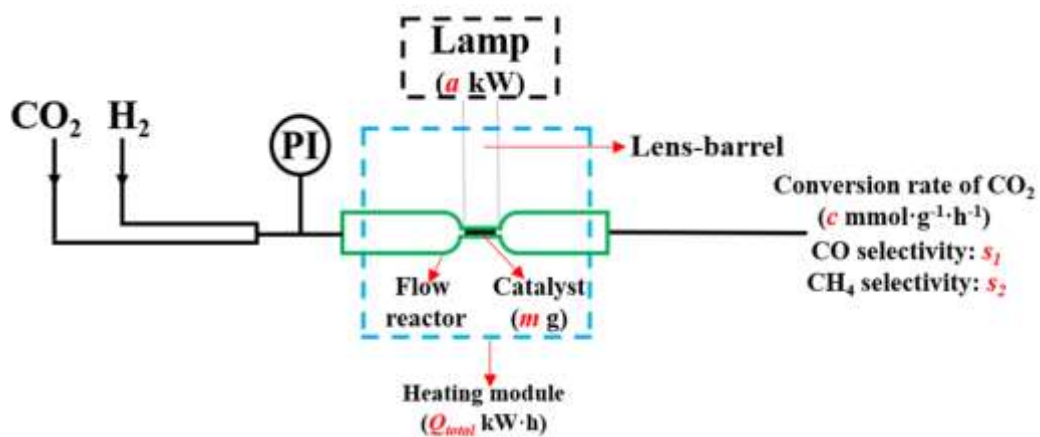


Figure S8. The major components, auxiliary equipment, and key parameters for a typical flow reactor.

In a typical experiment with a flow reactor, the gaseous reactants are continuously fed into the reactor. A lamp or a heating module is utilized to drive the reaction.

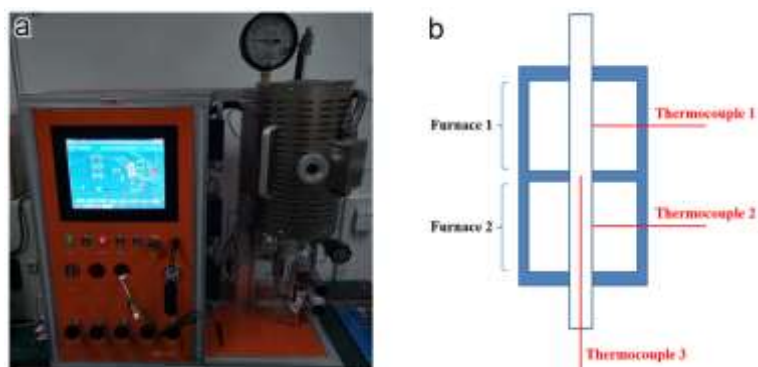


Figure S9. The flow reactor in our laboratory. (a) The photo of the practical facility.

(b) The structural diagram of the furnace. The heating module in our flow reactor consists of two combined furnaces in which the temperature is reflected and controlled by thermocouple 1 and 2. The catalyst is put in between these two furnaces.

The temperature of the catalyst is detected by thermocouple 3.

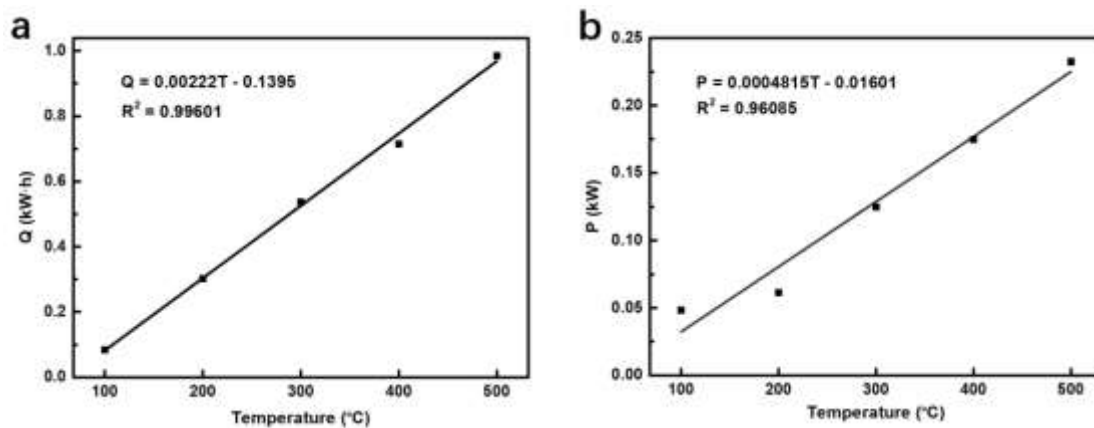


Figure S10. The power consumed in the (a) initial heating process and (b) the plateau region for maintaining the final temperature for our flow reactor.

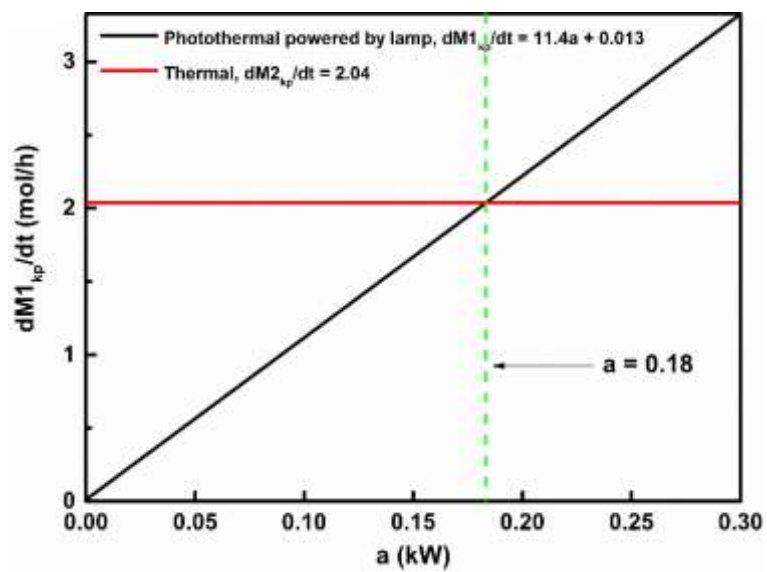


Figure S11. The dependence of net CO₂ reduction rate on the power of the lamp for flow reactors.

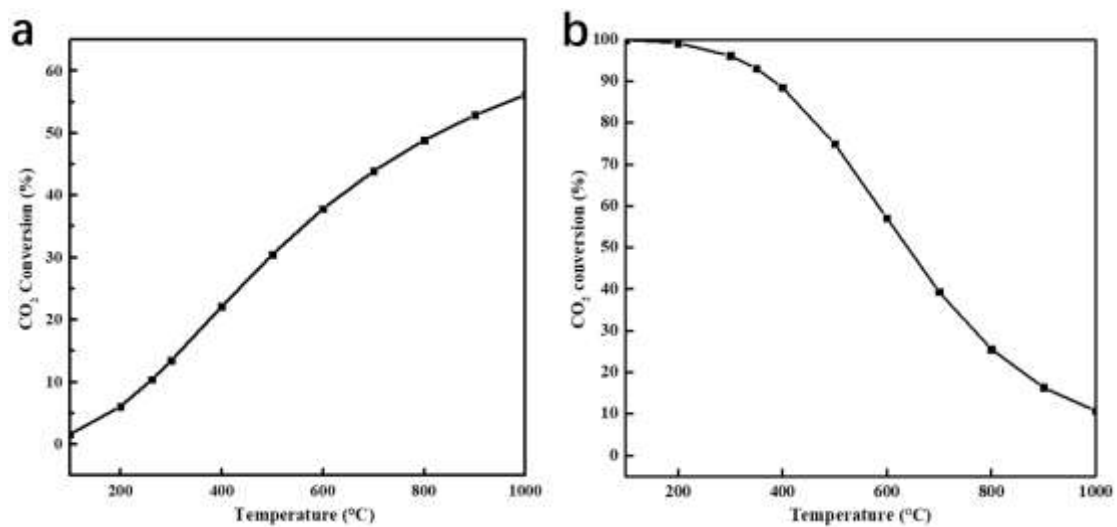


Figure S12. The ideal equilibrium conversion efficiency of CO₂ under different temperatures for (a) RWGS and (b) Sabatier reactions performed on flow reactors calculated from Aspen. CO₂: H₂ = 1:4.

Table S1. The key parameters of one typical case of photothermal catalytic performance for the demonstration of the calculation of net CO₂ reduction in batch reactors.^[1]

Catalysts	m (g) ^a	n (mol) ^b	s ₁ ^c	s ₂ ^d	t ₁ (h) ^e	c (mol·g ⁻¹ ·h ⁻¹) ^f	T (°C) ^g
Black In ₂ O ₃	0.12	0.0042	1	0	0.5	0.024	262

The values of m, n, and c were scaled up according to our batch reactor. ^am represents mass of the catalyst, ^bn represents the original feed amount of H₂ in a cycle, ^cs₁ represents selectivity of CO, ^ds₂ represents selectivity of CH₄, ^et₁ represents light irradiation time in a cycle, ^fc represents conversion rate of CO₂, ^gT represents the equilibrium temperature of the catalyst under illumination.

Table S2. Typical cases of photothermal catalytic CO₂ hydrogenation. Here we only list the representative works which reported both the light intensity and the corresponding temperature.

Reaction system	Catalyst	Light intensity (mW/cm ²)	T (°C) ^a	CO ₂ con. ^b	Ref
Batch	Ru/SiNW	14.5	117	0.8 mmol·g _{Ru} ⁻¹ ·h ⁻¹	[2]
Flow	Ru@FL-LDHs	10	350	96.3%	[3]
Batch	CoFeAl-LDH	52	310	78.6%	[4]
Flow	Ni/Y ₂ O ₃	1	288	80%	[5]
Flow	FeO–CeO ₂	22	446	43.63%	[6]
Batch	Black In ₂ O ₃	20	262	23.88 mmol·g ⁻¹ ·h ⁻¹	[1]
Batch	Co-PS@SiO ₂	20	383	612.4 mmol·g _{Co} ⁻¹ ·h ⁻¹	[7]

^aThe temperature of the catalyst under illumination. ^bThe CO₂ con. represents the conversion rate or efficiency of CO₂ when the unit is “mmol·g⁻¹·h⁻¹” or “%”, respectively.

Table S3. The key parameters of one typical case for photothermal catalytic performance of flow reactors.^[3]

Catalysts	m (g) ^a	n (mol) ^b	s ₁ ^c	s ₂ ^d	c (mol·g ⁻¹ ·h ⁻¹) ^e	T (°C) ^f
Ru@FL-LDHs	0.15	0.055	0	1	0.087	350

^a*m* represents mass of the catalyst, ^b*n* represents the original feed amount of H₂ in a cycle, ^c*s*₁ represents selectivity of CO, ^d*s*₂ represents selectivity of CH₄, ^e*c* represents conversion rate of CO₂, ^f*T* represents the equilibrium temperature of the catalyst under illumination.

Table S4. The exchange of energy during the catalytic reactions.

Reaction system	The electrical power consumed in the photothermal process	The electrical power consumed in the thermal process	Q_{sum} (J)^c
Batch ^a	38988000 J (10.83 kWh)	38126888 J (10.59 kWh)	5668.35 J (0.001575 kWh)
Flow ^b	54000000 J (15 kWh)	57200400 J (15.89 kWh)	-234750.24 J (-0.065 kWh)

All the calculations are based on the cases and facilities described above. ^aThe exchange of energy on batch reactors was calculated based on 100 cycles. ^bThe exchange of energy on flow reactors was calculated based on 100 hours. ^cThe total energy variation of the reaction gases at T . $Q_{sum} = Q_{ab}(T1-T2) + H^\theta$. $Q_{ab}(T1-T2)$: The absorbed energy of the gas mixture in the heating process from $T1$ to $T2$. H^θ : The enthalpy change during the reaction at T .

Since Q_{sum} is much lower than the consumed electrical power for both batch and flow reactors, it was neglected in all the calculations above.

Nevertheless, Q_{sum} might still need to be considered for cases with higher pressure or higher gas hourly space velocity (GHSV) in which the feed amount of reactant gases is much larger than that discussed above.

References

- [1] L. Wang, Y. Dong, T. Yan, Z. Hu, A. A. Jelle, D. M. Meira, P. N. Duchesne, J. Y. Y. Loh, C. Qiu, E. E. Storey, Y. Xu, W. Sun, M. Ghousoub, N. P. Kherani, A. S. Helmy, G. A. Ozin, *Nat. Commun.* **2020**, *11*, 2432.
- [2] P. G. O'Brien, A. Sandhel, T. E. Wood, A. A. Jelle, L. B. Hoch, D. D. Perovic, C. A. Mims, G. A. Ozin, *Adv. Sci.* **2014**, *1*, 1400001.
- [3] J. Ren, S. Ouyang, H. Xu, X. Meng, T. Wang, D. Wang, J. Ye, *Adv. Energy Mater.* **2017**, *7*, 1601657.
- [4] G. Chen, R. Gao, Y. Zhao, Z. Li, G. I. N. Waterhouse, R. Shi, J. Zhao, M. Zhang, L. Shang, G. Sheng, X. Zhang, X. Wen, L.-Z. Wu, C.-H. Tung, T. Zhang, *Adv. Mater.* **2018**, *30*, 1704663.
- [5] Y. Li, J. Hao, H. Song, F. Zhang, X. Bai, X. Meng, H. Zhang, S. Wang, Y. Hu, J. Ye, *Nat. Commun.* **2019**, *10*, 2359.
- [6] J. Zhao, Q. Yang, R. Shi, G. I. N. Waterhouse, X. Zhang, L.-Z. Wu, C.-H. Tung, T. Zhang, *NPG Asia Mater.* **2020**, *12*, 5.
- [7] K. Feng, S. H. Wang, D. K. Zhang, L. Wang, Y. Y. Yu, K. Feng, Z. Li, Z. J. Zhu, C. R. Li, M. J. Cai, Z. Y. Wu, N. Kong, B. H. Yan, J. Zhong, X. H. Zhang, G. A. Ozin, L. He, *Adv. Mater.* **2020**, *32*, 8.