

## Metal halide perovskites as an emergent catalyst for CO<sub>2</sub> photoreduction: a minireview

Melissa Méndez-Galván<sup>a</sup>, Brenda Alcántar-Vázquez<sup>b\*</sup>, Gabriela Diaz<sup>a</sup>, Illich A. Ibarra<sup>c</sup>, and Hugo A. Lara-García<sup>a\*</sup>

<sup>a</sup>Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, Ciudad de México, México.

<sup>b</sup>Instituto de Ingeniería, Coordinación de Ingeniería Ambiental, Universidad Nacional Autónoma de México, Circuito Escolar s/n, CU, Alcaldía Coyoacán, CP 04510, Ciudad de México, México.

<sup>c</sup> Laboratorio de Fisicoquímica y Reactividad de Superficies (LaFReS), Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, 04510, Ciudad de México, México.

## Electronic Supplementary Information

Table S1. Reaction parameters involved and the reaction product rates or yields of all the works reported.

Material	Solvents	Light source	Reaction time (h)	Reaction products	CO yield (μmol g <sup>-1</sup> )	CH <sub>4</sub> Yield (μmol g <sup>-1</sup> )	H <sub>2</sub> Yield (μmol g <sup>-1</sup> )	CO rate (μmol g <sup>-1</sup> h <sup>-1</sup> )	CH <sub>4</sub> rate (μmol g <sup>-1</sup> h <sup>-1</sup> )
CsPbBr <sub>3</sub> Fe: CsPbBr <sub>3</sub> <sup>1</sup>	Ethyl acetate/water	450 W, Xe lamp, 150 Mw cm <sup>-2</sup>	3	CO and CH <sub>4</sub>	-	-		4.6 3.2	1.9 6.1
CsPbBr <sub>3</sub> CsPb(Br <sub>0.7</sub> /Cl <sub>0.3</sub> ) <sub>3</sub> CsPb(Br <sub>0.5</sub> /Cl <sub>0.5</sub> ) <sub>3</sub> CsPb(Br <sub>0.3</sub> /Cl <sub>0.7</sub> ) <sub>3</sub> CsPbCl <sub>3</sub> <sup>2</sup>	Ethyl acetate	300 W, Xe lamp, 200 Mw cm <sup>-2</sup>	9	CO and CH <sub>4</sub>	135 156 767 204 65	60 72 108 63 31		15.0 17.3 85.2 22.7 7.2	6.7 8.0 12.0 7.0 3.4
Polyedron/CsPbBr <sub>3</sub> Hexapod/CsPbBr <sub>3</sub>	Ethyl acetate/water		4		130.7	58.8		-	-

Cube/CsPbBr <sub>3</sub> <sup>3</sup>		450 W, Xe lamp, 150 Mw cm <sup>-2</sup>		CO and CH <sub>4</sub>	16.4	7.6			
CsPbBr <sub>3</sub> /Cs <sub>4</sub> PbBr <sub>6</sub> Co <sub>0.5%</sub> @CsPbBr <sub>3</sub> /Cs <sub>4</sub> PbBr <sub>6</sub> Co <sub>1%</sub> @CsPbBr <sub>3</sub> /Cs <sub>4</sub> PbBr <sub>6</sub> Co <sub>2%</sub> @CsPbBr <sub>3</sub> /Cs <sub>4</sub> PbBr <sub>6</sub> Co <sub>3%</sub> @CsPbBr <sub>3</sub> /Cs <sub>4</sub> PbBr <sub>6</sub> <sup>4</sup>	Water	300 W, Xe lamp, 100 mw cm <sup>-2</sup>	20	CO and CH <sub>4</sub>	48 95 175 239 148	7 7 7 7 7		-	-
11.6nm-CsPbBr <sub>3</sub> 8.5nm-CsPbBr <sub>3</sub> 6.1nm-CsPbBr <sub>3</sub> 3.8nm-CsPbBr <sub>3</sub> <sup>5</sup>	Ethyl acetate/water	300 W, Xe lamp	8	CO and CH <sub>4</sub>	24 34 28 18	9 12 10 7		-	-
CsPbBr <sub>3</sub> Mn(4:1):CsPb(Br/Cl) <sub>3</sub> Mn (2:1):CsPb(Br/Cl) <sub>3</sub> Mn(2:3):CsPb(Br/Cl) <sub>3</sub> Mn(3:7):CsPb(Br/Cl) <sub>3</sub> <sup>6</sup>	Ethyl acetate	300 W, Xe lamp	9	CO and CH <sub>4</sub>	140 767 1917 1732 164	59 108 82 63 47			
CsPbBr <sub>3</sub> Cs <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> <sup>7</sup>	Dried octadecene	AM 1.5 G	4	CO	50 510	- -			
Cs <sub>2</sub> AgBiBr <sub>6</sub> NCs Washed Cs <sub>2</sub> AgBiBr <sub>6</sub> NCs <sup>8</sup>	Ethyl acetate	100 W, Xe lamp	6	CO and CH <sub>4</sub>	5.5 14.1	0.65 9.6			
Rb <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> <sup>9</sup>	Trichloroethane	32 W, UV lamp	10	CO and CH <sub>4</sub>	18.2 77.6 7.2	17.0 14.9 9.8			
Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> Cs <sub>3</sub> Bi <sub>2</sub> Cl <sub>9</sub> <sup>10</sup>	Multiple solvents	300 W, Xe lamp AM 1.5 G	5	CO	134.7 83.06			26.95 21.01	
CsPbBr <sub>3</sub> CsPbBr <sub>3</sub> /BP (1.0 %wt) CsPbBr <sub>3</sub> /BP (5.0 %wt) CsPbBr <sub>3</sub> /BP (10.0 %wt) BP <sup>11</sup>	Ethyl acetate/water	200 W, Xe lamp, 200 Mw cm <sup>-2</sup>	3	CO and CH <sub>4</sub>	31 80 134 70 19	13 30 32 9 3			
CsPbBr <sub>3</sub> Bi <sub>2</sub> WO <sub>6</sub> CsPbBr <sub>3</sub> Bi <sub>2</sub> WO <sub>6</sub> (1:1) CsPbBr <sub>3</sub> Bi <sub>2</sub> WO <sub>6</sub> (1:2) CsPbBr <sub>3</sub> Bi <sub>2</sub> WO <sub>6</sub> (1:5) CsPbBr <sub>3</sub> Bi <sub>2</sub> WO <sub>6</sub> (1:8)	Ethyl acetate/water	300 W, Xe lamp, 100 mw cm <sup>-2</sup>	10	CO and CH <sub>4</sub>	50 0 290 320 503 350	5 40 10 17 20 20			

CsPbBr <sub>3</sub> Bi <sub>2</sub> WO <sub>6</sub> (1:10) <sup>12</sup>					240	17		
CsPbBr <sub>3</sub> α-Fe <sub>2</sub> O <sub>3</sub> CsPbBr <sub>3</sub> /α-Fe <sub>2</sub> O <sub>3</sub> CsPbBr <sub>3</sub> /USGO CsPbBr <sub>3</sub> /USGO/α-Fe <sub>2</sub> O <sub>3</sub> <sup>13</sup>	Acetonitrile/water	Simulated Sunlight	4	CO			3.7 0.0 5.8 14.6 73.8	
TiO <sub>2</sub> TiO <sub>2</sub> /0.5CsPbBr <sub>3</sub> TiO <sub>2</sub> /1CsPbBr <sub>3</sub> TiO <sub>2</sub> /2CsPbBr <sub>3</sub> TiO <sub>2</sub> /3CsPbBr <sub>3</sub> TiO <sub>2</sub> /4CsPbBr <sub>3</sub> CsPbBr <sub>3</sub> <sup>14</sup>	Acetonitrile/water	300 W, Xe lamp	1	CO and H <sub>2</sub>	6.6 7.97 11.45 13.49 11.33 9.89 6.2		0.1 0.11 0.23 0.43 0.28 0.28 0.0	
CsPbBr <sub>3</sub> QDs CsPbBr <sub>3</sub> QD/GO <sup>15</sup>	Ethyl acetate	100 W, Xe lamp, 150 mW cm <sup>-2</sup>	12	CO and CH <sub>4</sub>	49.5 58.7	22.9 29.6		
ZIF-8 ZIF-67 CsPbBr <sub>3</sub> CsPbBr <sub>3</sub> @ ZIF-8 CsPbBr <sub>3</sub> @ ZIF-67 <sup>16</sup>	Water	100 W, Xe lamp	3	CO and CH <sub>4</sub>	0 1.5 1 1.3 1.5	2 3 3.5 5 10		
CsPbBr <sub>3</sub> QDs g-C <sub>3</sub> N <sub>4</sub> 10-g-C <sub>3</sub> N <sub>4</sub> /CsPbBr <sub>3</sub> QDs 20- g-C <sub>3</sub> N <sub>4</sub> /CsPbBr <sub>3</sub> QDs 30- g-C <sub>3</sub> N <sub>4</sub> /CsPbBr <sub>3</sub> QDs <sup>17</sup>	Ethyl acetate/water or acetonitrile /water	300 W, Xe lamp	2	CO			12/20 30/42 40/80 70/149 50/120	
CsPbBr <sub>3</sub> QDs CsPbBr <sub>3</sub> 5%-UiO-66(NH <sub>2</sub> )-CsPbBr <sub>3</sub> 10%-UiO-66(NH <sub>2</sub> )-CsPbBr <sub>3</sub> 15%-UiO-66(NH <sub>2</sub> )-CsPbBr <sub>3</sub> 30%-UiO-66(NH <sub>2</sub> )-CsPbBr <sub>3</sub> <sup>18</sup>	Ethyl acetate/water	300 W, Xe lamp		CO and CH <sub>4</sub>	40 15 62 80 100 70	12 0 2 3 3 3		
CsPbBr <sub>3</sub> NC, CsPbBr <sub>3</sub> NC/MRGO CsPbBr <sub>3</sub> NC/BZNW/MRGO <sup>19</sup>	Water	150 W, Xe lamp AM 1.5 G	3	CO and CH <sub>4</sub>	2 2.7 3.8	3.7 11 19		10.44 31.52 52.02
CN CsPbBr <sub>3</sub> 2Br-CN 3Br-2CN	Acetonitrile/water	300 W, Xe lamp	2	CO			5.5 5.0 7.4 28.5	

Br-CN Br-4CN <sup>20</sup>								25.2 10.6	
CsPbBr <sub>3</sub> Ni(tpy) CsPbBr <sub>3</sub> -0.06Ni(tpy) CsPbBr <sub>3</sub> -0.12Ni(tpy) CsPbBr <sub>3</sub> -0.24Ni(tpy) CsPbBr <sub>3</sub> -0.48Ni(tpy) <sup>21</sup>	Ethyl acetate/water	300 W, Xe lamp, 100 mw cm <sup>-2</sup>	4	CO and CH <sub>4</sub>	50 0 780 150 1600 1490	0 0 40 50 60 55			
CsPbBr <sub>3</sub> TiO-CN CsPbBr <sub>3</sub> @CN CsPbBr <sub>3</sub> @TiO-CN <sup>22</sup>	Ethyl acetate/water	300 W, Xe lamp	10	CO	20 40 50 129				
PCN-221 MAPbI <sub>3</sub> @PCN-221 PCN-221(Fe <sub>0.2</sub> ) MAPbI <sub>3</sub> @PCN-221(Fe <sub>0.2</sub> ) PCN-221(Fe <sub>0.4</sub> ) MAPbI <sub>3</sub> @PCN-221(Fe <sub>0.4</sub> ) PCN-221(Fe <sub>0.6</sub> ) MAPbI <sub>3</sub> @PCN-221(Fe <sub>0.6</sub> ) PCN-221(Fe <sub>0.8</sub> ) MAPbI <sub>3</sub> @PCN-221(Fe <sub>0.8</sub> ) PCN-221(Fe) MAPbI <sub>3</sub> @PCN-221(Fe) <sup>23</sup>	Ethyl acetate/water	300 W, Xe lamp 100 mw cm <sup>-2</sup>	25	CO and CH <sub>4</sub>	15 20 35 104 40 160 20 250 15 300 10 360	0 0 40 445 50 450 50 440 50 460 50 500			
CsPbBr <sub>3</sub> CsPbBr <sub>3</sub> /MoS <sub>2</sub> , (0.25%) CsPbBr <sub>3</sub> /MoS <sub>2</sub> , (0.5%) CsPbBr <sub>3</sub> /MoS <sub>2</sub> , (1.0%) CsPbBr <sub>3</sub> /MoS <sub>2</sub> , (2.0%) CsPbBr <sub>3</sub> /MoS <sub>2</sub> , (1.5%) CsPbBr <sub>3</sub> /MoS <sub>2</sub> , (2.5%) CsPbBr <sub>3</sub> /MoS <sub>2</sub> , (5.0%}) MoS <sub>2</sub> <sup>24</sup>	Ethyl acetate	200 W, Xe lamp, 200 mw cm <sup>-2</sup>	30	CO and CH <sub>4</sub>	27 30 58 70 27 18 15 9 5	10 12 19 30 49 35 22 7 3			
CsPbBr <sub>3</sub> MIL-100(Fe) CsPbBr <sub>3</sub> / MIL-100(Fe) <sup>25</sup>	Water	300 W, Xe lamp (>420 nm)	4	CO				9 10 41	
CsPbBr <sub>3</sub> CTF-1 CsPbBr <sub>3</sub> / CTF-1	Ethyl acetate	300 W, Xe lamp (>400 nm)	4	CO				9.7 13 48.2	

CsPbBr <sub>3</sub> / CTF-1-Ni <sup>26</sup>							86.5		
CsPbBr <sub>3</sub> CsPbBr <sub>3</sub> CsPbBr <sub>3</sub> CsPbBr <sub>3</sub> CsPbBr <sub>3</sub> /Pt <sup>27</sup>	Toluene Ethyl acetate Iso-propanol Acetonitrile Ethyl acetate	150 W, Xe lamp	6	CO, CH <sub>4</sub> and H <sub>2</sub>	0.33 4.21 0.01 0.57 1.6	0 0.86 0.75 0 9	0 0.39 0.43 0 1.8		
CsPbBr <sub>3</sub> C/Cs <sub>4</sub> PbBr <sub>6</sub> CsPbBr <sub>3</sub> /Cs <sub>4</sub> PbBr <sub>6</sub> Co <sub>0.5%</sub> @CsPbBr <sub>3</sub> /Cs <sub>4</sub> PbBr <sub>6</sub> Co <sub>1%</sub> @CsPbBr <sub>3</sub> /Cs <sub>4</sub> PbBr <sub>6</sub> Co <sub>2%</sub> @CsPbBr <sub>3</sub> /Cs <sub>4</sub> PbBr <sub>6</sub> <sup>28</sup>	Acetonitrile /water/methanol Acetonitrile /water Acetonitrile /water/methanol Acetonitrile /water/methanol Acetonitrile /water/methanol Acetonitrile /water/methanol	300 W, Xe lamp, 100 mw cm <sup>-2</sup>	15	CO	2.58 µmol 2.69 µmol 2.96 µmol 7.21 µmol 7.34 µmol 7.28 µmol				
NS CsPbBr <sub>3</sub> NS CsPbBr <sub>3</sub> – RGO Cu-RGO Ex situ NS CsPbBr <sub>3</sub> – Cu-RGO NS CsPbBr <sub>3</sub> – Cu-RGO NR1 CsPbBr <sub>3</sub> – Cu-RGO NR2 CsPbBr <sub>3</sub> – Cu-RGO <sup>29</sup>	Water	300 W, Xe lamp, 100 mw cm <sup>-2</sup>	4	CO, CH <sub>4</sub> and H <sub>2</sub>				2.5 3 0 0.8 0.5 0.5 0.5	0.5 0.5 1 7.5 12.5 6 9
CsPbBr <sub>3</sub> NC CsPbBr <sub>3</sub> NC/Pd NS (100) CsPbBr <sub>3</sub> NC/Pd NS (300) CsPbBr <sub>3</sub> NC/Pd NS (600) CsPbBr <sub>3</sub> NC/Pd NS (900) <sup>30</sup>	Water	150 W, Xe lamp, 150 mW cm <sup>-2</sup>	3	CO, CH <sub>4</sub> and H <sub>2</sub>	3.67 7.92 12.63 5.76 3.89	2.79 3.06 3.93 10.41 5.25	0 0.52 1.16 3.28 1.4		
CsPbBr <sub>3</sub> CsPbBr <sub>3</sub> -Au CsPbBr <sub>3</sub> CsPbBr <sub>3</sub> -Au <sup>31</sup>	Acetonitrile /propanol	100 W, Xe lamp, 100 mW cm <sup>-2</sup> (λ>420nm/λ>580 nm)		CO and CH <sub>4</sub>	5 10 0 1	0 5 0 .5			
CsPbBr <sub>3</sub> CsPbBr <sub>3</sub> Re(300) CsPbBr <sub>3</sub> Re(600) CsPbBr <sub>3</sub> Re(900) <sup>32</sup>	Tolueno/Isopropanol	150 W, Xe lamp, 150 mW cm <sup>-2</sup>	3	CO, CH <sub>4</sub> and H <sub>2</sub>	2 30 100 80	0 0 0 0	0 2 5 7		
CsPbBr <sub>3</sub> NCs/MXene-20 <sup>33</sup>	Ethyl acetate	300 W, Xe lamp	5	CO and CH <sub>4</sub>	- 140	- 35		26.3 -	- 7.25

## References

- 1 S. Shyamal, S. K. Dutta and N. Pradhan, *J. Phys. Chem. Lett.*, 2019, **10**, 7965–7969.
- 2 S. H. Guo, J. Zhou, X. Zhao, C. Y. Sun, S. Q. You, X. L. Wang and Z. M. Su, *J. Catal.*, 2019, **369**, 201–208.
- 3 S. Shyamal, S. K. Dutta, T. Das, S. Sen, S. Chakraborty and N. Pradhan, *J. Phys. Chem. Lett.*, 2020, **11**, 3608–3614.
- 4 Y. F. Mu, W. Zhang, X. X. Guo, G. X. Dong, M. Zhang and T. B. Lu, *ChemSusChem*, 2019, **12**, 4769–4774.
- 5 J. Hou, S. Cao, Y. Wu, Z. Gao, F. Liang, Y. Sun, Z. Lin and L. Sun, *Chem. - A Eur. J.*, 2017, **23**, 9481–9485.
- 6 Yu-Wei Liu et al, *Nanotechnology*, 2020, **in press**, 0–31.
- 7 C. Lu, D. S. Itanze, A. G. Aragon, X. Ma, H. Li, K. B. Ucer, C. Hewitt, D. L. Carroll, R. T. Williams, Y. Qiu and S. M. Geyer, *Nanoscale*, 2020, **12**, 2987–2991.
- 8 L. Zhou, Y. F. Xu, B. X. Chen, D. Bin Kuang and C. Y. Su, *Small*, 2018, **14**, 1–7.
- 9 S. S. Bhosale, A. K. Kharade, E. Jokar, A. Fathi, S. M. Chang and E. W. G. Diau, *J. Am. Chem. Soc.*, 2019, **141**, 20434–20442.
- 10 J. Sheng, Y. He, J. Li, C. Yuan, H. Huang, S. Wang, Y. Sun, Z. Wang and F. Dong, *ACS Nano*, 2020, **14**, 13103–13114.
- 11 X. Wang, J. He, J. Li, G. Lu, F. Dong, T. Majima and M. Zhu, *Appl. Catal. B Environ.*, 2020, **277**, 119230.
- 12 J. Wang, J. Wang, N. Li, X. Du, J. Ma, C. He and Z. Li, *ACS Appl. Mater. Interfaces*, , DOI:10.1021/acsami.0c08152.
- 13 Y. Mu, W. Zhang, G. Dong, K. Su, M. Zhang and T. Lu, 2020, **2002140**, 1–8.
- 14 J. X. & J. Y. Feiyan Xu, Meng , Bei Cheng , Shengyao Wang, 2020, 1–9.
- 15 Y. F. Xu, M. Z. Yang, B. X. Chen, X. D. Wang, H. Y. Chen, D. Bin Kuang and C. Y. Su, *J. Am. Chem. Soc.*, 2017, **139**, 5660–5663.

- 16 Z. C. Kong, J. F. Liao, Y. J. Dong, Y. F. Xu, H. Y. Chen, D. Bin Kuang and C. Y. Su, *ACS Energy Lett.*, 2018, **3**, 2656–2662.
- 17 S. Wan, M. Ou, Q. Zhong and X. Wang, *Chem. Eng. J.*, 2019, **358**, 1287–1295.
- 18 M. Ou, W. Tu, S. Yin, W. Xing, S. Wu, H. Wang, S. Wan, Q. Zhong and R. Xu, *Angew. Chemie*, 2018, **130**, 13758–13762.
- 19 Y. Jiang, J. F. Liao, Y. F. Xu, H. Y. Chen, X. D. Wang and D. Bin Kuang, *J. Mater. Chem. A*, 2019, **7**, 13762–13769.
- 20 R. Cheng, H. Jin, M. B. J. Roeffaers, J. Hofkens and E. Debroye, *ACS Omega*, 2020, **5**, 24495–24503.
- 21 Z. Chen, Y. Hu, J. Wang, Q. Shen, Y. Zhang, C. Ding, Y. Bai, G. Jiang, Z. Li and N. Gaponik, *Chem. Mater.*, 2020, **32**, 1517–1525.
- 22 X. Guo, S. Tang, Y. Mu, L. Wu, G. Dong and M. Zhang, *RSC Adv.*, 2019, **9**, 34342–34348.
- 23 L. Wu, Y. Mu, X. Guo, W. Zhang, Z. Zhang, M. Zhang and T. Lu, 2019, 9491–9495.
- 24 X. Wang, J. He, L. Mao, X. Cai, C. Sun and M. Zhu, *Chem. Eng. J.*, 2020, 128077.
- 25 M.-F. Composites, *Catalysts*, 2020, **100**, 1–13.
- 26 Q. Wang, J. Wang, J. C. Wang, X. Hu, Y. Bai, X. Zhong and Z. Li, *ChemSusChem*, 2021, **230026**, 1131–1139.
- 27 Y. X. Chen, Y. F. Xu, X. D. Wang, H. Y. Chen and D. Bin Kuang, *Sustain. Energy Fuels*, 2020, **4**, 2249–2255.
- 28 G. X. Dong, W. Zhang, Y. F. Mu, K. Su, M. Zhang and T. B. Lu, *Chem. Commun.*, 2020, **56**, 4664–4667.
- 29 S. Kumar, M. Regue, M. A. Isaacs, E. Freeman and S. Eslava, *ACS Appl. Energy Mater.*, 2020, **3**, 4509–4522.
- 30 Y. F. Xu, M. Z. Yang, H. Y. Chen, J. F. Liao, X. D. Wang and D. Bin Kuang, *ACS Appl. Energy Mater.*, 2018, **1**, 5083–5089.
- 31 J.-F. Liao, Y.-T. Cai, J.-Y. Li, Y. Jiang, X.-D. Wang, H.-Y. Chen and D.-B. Kuang, *J. Energy Chem.*, 2021, **53**, 309–315.
- 32 Z. C. Kong, H. H. Zhang, J. F. Liao, Y. J. Dong, Y. Jiang, H. Y. Chen and D. Bin Kuang, *Sol. RRL*, 2020, **4**, 1–7.
- 33 A. Pan, X. Ma, S. Huang, Y. Wu, M. Jia, Y. Shi, Y. Liu, P. Wangyang, L. He and Y. Liu, *J. Phys. Chem. Lett.*, 2019, **10**, 6590–6597.