

## **Nanomaterials as Catalysts for CO<sub>2</sub> Transformation into Value-added products: A Review**

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Table S1. Summary of CO<sub>2</sub> Photoreduction using various metallic nanophotocatalysts

Catalyst	Source	Reaction conditions	Products yields and selectivity	Ref.
ZnO ( <b>Z-1</b> ), Co-doped ZnO ( <b>Z-2</b> ), Co-doped ZnO/rGO ( <b>Z-3</b> )	400 W Xe lamp	0.1 g/250 mL catalyst; photocatalytic reduction experiments for 7h; room temperature, pH=7.5	7.5 $\mu\text{mol/g}_{\text{cat}}$ 27.3 $\mu\text{mol/g}_{\text{cat}}$ 30.1 $\mu\text{mol/g}_{\text{cat}}$	(M. Mgolombane et al., 2021)
Co-doped TiO <sub>2</sub> Co-doped TiO <sub>2</sub> /rGO	500 W Xe lamp	0.1 mg catalyst, pH=7.5; room temperature; 7 h; batch reactor using CO <sub>2</sub> and H <sub>2</sub> O molecule.	CH <sub>3</sub> OH 180 $\mu\text{mol/g}_{\text{cath}}$	(Mvano Mgolombane et al., 2021)
GaP	Halogen lamp at 365 nm	Electrode consisting of single crystal GaP in 0.05 M K <sub>2</sub> HPO <sub>4</sub> /KH <sub>2</sub> PO <sub>4</sub> at 25 °C (38 hours)	HCOOH: 1.2 x 10 <sup>-2</sup> M HCHO: 3.2 x 10 <sup>-4</sup> M CH <sub>3</sub> OH: 1.1 x 10 <sup>-4</sup> M	(Gaya and Abdullah, 2008)
TiO <sub>2</sub> , ZnO, CdS, GaP, SiC, WO <sub>3</sub>	500 W Xe lamp	Aqueous suspension of semiconductor in water at room temperature (2 hours)	<b>TiO<sub>2</sub></b> HCOOH: 1.8 x 10 <sup>-3</sup> M CH <sub>3</sub> OH: 14.6 x 10 <sup>-4</sup> M <b>ZnO</b> HCOOH: 1.2 x 10 <sup>-3</sup> M CH <sub>3</sub> OH: 3.5 x 10 <sup>-4</sup> M <b>CdS</b> HCOOH: 2.0 x 10 <sup>-3</sup> M CH <sub>3</sub> OH: 11.7 x 10 <sup>-4</sup> M	(Bhatkhande et al., 2002)

			<p><b>GaP</b> HCOOH: 1.0 x 10<sup>-3</sup> M CH<sub>3</sub>OH: 11.0 x 10<sup>-4</sup> M</p> <p><b>SiC</b> HCOOH: 1.0 x 10<sup>-3</sup> M CH<sub>3</sub>OH: 53.5 x 10<sup>-4</sup> M</p> <p><b>WO<sub>3</sub></b> HCOOH: 0 CH<sub>3</sub>OH: 0</p>	
Nd <sub>2</sub> O <sub>3</sub> doped BaTiO <sub>3</sub>	High pressure Hg lamp	Aqueous suspensions at 65 °C	HCHO: 0.027 μmol Yield (%):0.0045	(Wang et al., 2010)
p-GaP, p-GaAs	150 W Xe lamp	Electrodes in 0.5 M Na <sub>2</sub> CO <sub>3</sub> Single crystal at 25 °C (pH 6.3-6.5)	<p><b>p-GaP</b> HCOOH: 670 μmol HCHO: 13 μmol CH<sub>3</sub>OH: 10 μmol</p> <p><b>p-GaAs</b> HCOOH: 320 μmol HCHO: 5 μmol</p>	(Slamet et al., 2005)
RuO <sub>2</sub> doped TiO <sub>2</sub>	High pressure Hg lamp	Aqueous suspension in water at 60 °C (48 hours)	HCOOH: 1.46 μmol/h <b>Major product:</b> HCHO- 0.18 μmol/h	(Zhang et al., 2009)

			CH <sub>3</sub> OH: 0.2 μmol/h	
Cd-loaded ZnS	High pressure Hg lamp	Aqueous suspension in 1.5 x 10 <sup>-3</sup> M NaHCO <sub>3</sub> at room temperature (pH 5.5)	<b>Quantum efficiency</b> HCOOH: 32.5% <b>Major product</b> HCHO: 42.0% H <sub>2</sub> : 5.0%	(Halmann, 1978)
ZnS	High pressure Hg lamp	Colloidal suspension in 0.7 M NaH <sub>2</sub> PO <sub>2</sub> at 20 °C (pH 7) for 5 hours	HCOOH: 75.1 μmol/h CO: 2.7 μmol/h <b>Major product</b> H <sub>2</sub> : 86.0 μmol/h	(Halmann, 1978)
ZnS-loaded SiO <sub>2</sub>	Tungsten halogen Lamp (~350 nm)	Aqueous suspension in water at 25 °C (6 hours)	<b>Major product</b> HCOOH: 10 mmol	(Inoue et al., 1979)
ZnS	1000 W Xenon arc lamp	Aqueous suspension in 0.2 M NaHCO <sub>3</sub>	<b>Major product</b> HCOOH: 140 mmol formate/g cat-hr	(Ulman et al., 1982)
Au/TiO <sub>2</sub>	1000 W Xenon arc lamp	Aqueous suspension in 0.2 M NaHCO <sub>3</sub> at 25 °C (pH 9) for 8 hours	<b>Major product</b> HCOOH: 55 mmol formate/g cat-hr	(Halmann et al., 1984)
Ag/TiO <sub>2</sub>	1000 W Xenon arc lamp	Aqueous suspension in 0.2 M NaHCO <sub>3</sub> at room temperature.	<b>Major product</b> HCOOH: 3.89 mmol formate/g cat-hr	(Inoue et al., 1995)
TiN/TiO <sub>2</sub>	1000 W Xenon	Aqueous suspension in	<b>Major product</b> HCOOH: 3000	(Kanemoto et al., 1992)

	arc lamp	0.2 M NaHCO <sub>3</sub> at 22 °C for 8 hours	mmol formate/g cat-hr	
Ru NPS loaded into ZnS	150 W XBO Arc lamp	Aqueous suspension in water at 25 °C for 5 hours	HCOOH: 0.006 M	(Johne and Kisch, 1997)
ZnS microcrystallite	High pressure Hg lamp	Colloidal suspension in H <sub>3</sub> PO <sub>4</sub> at 25 °C (pH 7)	Major products HCOOH: 11.6 μmol HCHO: 11.8 μmol CH <sub>3</sub> OH: 1.2 μmol	(Pan et al., 2018)
CdS, ZnO, SiC, BaTiO <sub>3</sub> , SrTiO <sub>3</sub>	Medium pressure Hg lamp	Aqueous suspension in water at 25 °C (pH 4)	Major products HCOOH, HCHO	(Pan et al., 2017)
CdS, ZnS	Medium pressure Hg lamp	Aqueous suspension in water at 25 °C (pH 4) for 24 hours	<b>ZnS</b> Major product HCOOH: 320 μmol/L <b>CdS</b> Major product HCOOH: 87 μmol/L	(Pan and Heagy, 2019)
SiO <sub>2</sub> -stabilized ZnS	Medium pressure Hg lamp	Aqueous suspension in water at room temperature (pH 7)	Major product: HCOOH: 0.8% AQE	(Baran et al., 2015)

TiO <sub>2</sub>	990 W Xe lamp	Aqueous suspension in water at 293 K	Major product HCOOH: 8 x 10 <sup>-6</sup> mol/g-cat	(Duplessix et al., 1994)
TiO <sub>2</sub>	Xe lamp	Aqueous suspension in water at room temperature.	Major products HCOOH: 2.3 x 10 <sup>-6</sup> mol/g-cat CH <sub>4</sub> : 1.2 x 10 <sup>-6</sup> mol/g-cat	(Eggins et al., 1998)
TiO <sub>2</sub>	990 W Xe lamp	Power in supercritical fluid CO <sub>2</sub> in a stainless steel vessel at 9.0 MPa and 35°C.	Major product HCOOH: 9 x 10 <sup>-6</sup> mol/g-cat	(Kaneco ' et al., 1997)
CdS	500 W high pressure Hg arc lamp	Aqueous suspension in water and 2-propanol at 25 °C for 7 hours	Major products HCOOH: 0.4 μmol HCHO: 1.9 μmol CO: 0.8 μmol H <sub>2</sub> : 0.5 μmol	(Kaneco et al., 1998)
CdS-SiO <sub>2</sub> , CdS-ZnS	100 W tungsten halogen lamp, 150 W xenon lamp	Aqueous suspension in water	<b>CdS-SiO<sub>2</sub></b> Major products HCOOH: 10 x 10 <sup>-5</sup> M HCHO: 3.4 x 10 <sup>-5</sup> M <b>CdS-ZnS</b> Major product HCOOH: 4.5 x 10 <sup>-5</sup> M	(Kaneco et al., 1999)
<b>MnS</b>	450 W medium pressure UV	Aqueous suspension in water and 7.2 mM NaHS and 2.5 mM NaHCO <sub>3</sub> at 25 °C (pH 4) for 24 hours	Major product HCOOH: 200 μM	(Liu et al., 1998)

	Hg arc lamp			
<b>MWCNT supported TiO<sub>2</sub></b>	15 W UV lamp 365 nm	Aqueous suspension in water at 25 °C for 5 hours	Major products HCOOH: 125.1 μmol/g CH <sub>4</sub> : 73.33 μmol/g C <sub>2</sub> H <sub>5</sub> OH: 149.36 μmol/g	(Xia et al., 2007)
<b>Dye-sensitized TiO<sub>2</sub> film</b>	300 W Xe lamp	Electrode (Pt/FTO) in water at 25 °C (pH 4) for 24 hours	Major products HCOOH: 1.8mmol/cm <sup>2</sup> HCHO: 1.4 mmol/cm <sup>2</sup> CH <sub>3</sub> OH: 1.9 mmol/cm <sup>2</sup>	(Qin et al., 2013)
<b>Ti silicalite molecular sieve</b>	Pulsed Nd:YAG laser at 10 Hz ~ 266 nm	Methanol at 25 °C	Major products HCOOH, CO	(Ulagappan and Frei, 2000)
<b>N-doped Ta<sub>2</sub>O<sub>5</sub> (N-Ta<sub>2</sub>O<sub>5</sub>), linked with electrocatalysts [Ru(dcbpy)(bpy)(CO)<sub>2</sub>]<sup>2+</sup> or [Ru(dcbpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup></b>	Xe lamp	Ag/AgCl electrode (reference) and glass carbon electrode (counter). Aqueous suspension in MeCN/TEOA at 25 °C.	<b>Quantum yield</b> HCOOH: 1.9%	(Sato et al., 2010)

<b>InP/Ru complex polymer hybrid</b>	Solar simulator with AM 1.5 filter	Aqueous suspension in water and 10 mM NaHCO <sub>3</sub> at 25 °C.	Major product HCOOH: 4.71 mol/cm <sup>2</sup>	(Sato et al., 2011)
<b>Cu<sub>2</sub>ZnSnS<sub>4</sub></b>	Xe light source	Aqueous suspension in water at 25 °C.	>80% selectivity HCOOH: 0.22 mM	(Arai et al., 2011)
<b>N-doped Ta<sub>2</sub>O<sub>5</sub> With Ru(dcbpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup></b>	500 W Xe lamp	Aqueous suspension in acetonitrile/triethanolamine at 25 °C for 60 hours.	<b>Quantum efficiency</b> HCOOH: 1.9%	(Suzuki et al., 2011)
<b>Ag-loaded ALa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (A = Ca, Sr, Ba)</b>	400W high-pressure mercury lamp	Aqueous suspension in water at 25 °C for 7 hours.	BaLa <sub>4</sub> Ti <sub>4</sub> O <sub>15</sub> : Major product HCOOH: 150 μmol	(Iizuka et al., 2011)
<b>Co<sub>3</sub>O<sub>4</sub></b>	21 W LED Lamp (~510to 620 nm)	Aqueous suspension in water at at room temperature for 4 hours.	Major products HCOOH: 4.53 μmol/g-h HCHO: 0.62 μmol/g-h Trace amounts of CH <sub>4</sub> and CO	(Mendoza et al., 2012)
<b>BiYO<sub>3</sub></b>	300W Xe lamp	Aqueous suspension in 0.25 M NaOH and 0.1 M Na <sub>2</sub> SO <sub>3</sub> to maintain an alkaline environment). Temperature at 25 °C	Major product HCOOH: 1.68 μmol/L	(Qin et al., 2016)



<b>KHCO<sub>3</sub>Cu(II)-grafted Nb<sub>3</sub>O<sub>8</sub></b>	Xe-Hg lamp	Aqueous suspension in 0.5 M KHCO <sub>3</sub> at room temperature and pH adjusted to 12 using NaOH.	Major product CO: 1.5 μmol	(Yin et al., 2015)
<b>Cu-TiO<sub>2</sub></b>	300 W Xe lamp	Aqueous suspension in water at room temperature	Major product CO: 244 μmol/g No trace amounts	(Lan et al., 2019)
<b>ZnO-Cu<sub>2</sub>O nanoparticles</b>	300 W Xe lamp	Aqueous suspension in water and 0.2 M Na <sub>2</sub> CO <sub>3</sub> at room temperature (pH 7.4)	Major product (selectivity for >99%) CH <sub>4</sub> : 1080 μmol/g <sub>cat</sub> h Trace amounts of CO: 1.4 μmol/g <sub>cat</sub> h	(Bae et al., 2017)
<b>CuO</b>	5 W UVC lamp	Aqueous suspension in water (0.1 M Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , 0.1 M KBrO <sub>3</sub> , and 0.1 M NaOH) at room temperature for 24 hours.	Major product CH <sub>4</sub> : 1000 μmol/L-g Trace amount of CO: 6 μmol/L-g	(Nogueira et al., 2019)
<b>Cu<sub>2</sub>O/CNPs</b>	300 W Xenon lamp	Aqueous suspension in 1M NaOH under ambient conditions for 6 hours.	CH <sub>3</sub> OH: 236.43 μmol g <sup>-1</sup> cat	(Dedong et al., 2018)
<b>Ag-Cu<sub>2</sub>O/ZnO nanorods</b>	300 W Xe arc lamp	Aqueous suspension in water under ambient conditions.	Major product CO: 9.94 μmol/g	(Zhang et al., 2009)
<b>Cu<sub>2</sub>O/TiO<sub>2</sub></b>	1 kW high-pressure Hg (Xe) lamp	Aqueous suspension in water at room temperature (20 °C)	Major product CO: 2.11 μmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	(Zhang et al., 2020)
<b>Cu<sub>x</sub>O-TiO<sub>2</sub></b>	100 W Xenon solar	Powder photocatalyst with CO <sub>2</sub> at room temperature after 5 hours	Major product CH <sub>4</sub> : 221.6 ppm/g-h	(Park et al., 2016)

	simulator with AM 1.5 filter			
<b>AgCuInS<sub>2</sub>-Graphene-TiO<sub>2</sub></b>	Metal halide lamp of 500 W	100 mg of the photocatalyst; sacrificial scavenger (Na <sub>2</sub> SO <sub>3</sub> ) in 0.04 M NaHCO <sub>3</sub> for 48 hours at room temperature	Major product CH <sub>3</sub> OH: 14.35%	(Gusain et al., 2016)

Table S2: CO<sub>2</sub> reduction using photoelectrochemical method

<b>Catalyst</b>	<b>Source</b>	<b>Reaction conditions</b>	<b>Products yields and selectivity</b>	<b>Ref.</b>
Cu <sub>2</sub> O	1000 W Xenon arc lamp	Aqueous suspension in 0.2 M NaHCO <sub>3</sub> at 25 °C (8 hours)	<b>Major product</b> HCOOH: 2.78 mmol formate/g cat-hr	(Aurian-Blajeni et al., 1983)
Reduced titania-Cu <sub>2</sub> O	100 W solar simulator with AM 1.5 filter	CO <sub>2</sub> passing through solid photocatalyst at ambient temperature condition for 6 hours.	CH <sub>4</sub> : 462 nmol/g	(Ali et al., 2020)
Anodized titanium oxide nanotubes and Pd-decorated Bismuth titanate	300W solar simulator with AM 1.5 filter	Thin films submerged in 0.1 M H <sub>2</sub> SO <sub>4</sub> at 25 °C for 12 hours.	Major product HCOOH: 160 μmol/h/g	(Raja et al., 2011)

GaP	Halogen lamp at 365 nm	Electrode consisting of single crystal GaP in 0.05 M $K_2HPO_4/KH_2PO_4$ at 25 °C (38 hours)	HCOOH: 1.2 x $10^{-2}$ M HCHO: 3.2 x $10^{-4}$ M CH <sub>3</sub> OH: 1.1 x $10^{-4}$ M	(Gaya and Abdullah, 2008)
p-GaP, p-GaAs	150 W Xe lamp	Electrodes in 0.5 M Na <sub>2</sub> CO <sub>3</sub> Single crystal at 25 °C (pH 6.3-6.5)	<b>p-GaP</b> HCOOH: 670 $\mu$ mol HCHO: 13 $\mu$ mol CH <sub>3</sub> OH: 10 $\mu$ mol <b>p-GaAs</b> HCOOH: 320 $\mu$ mol HCHO: 5 $\mu$ mol	(Slamet et al., 2005)
Dye-sensitized TiO <sub>2</sub> film	300 W Xe lamp	Electrode (Pt/FTO) in water at 25 °C (pH 4) for 24 hours	Major products HCOOH: 1.8mmol/cm <sup>2</sup> HCHO: 1.4 mmol/cm <sup>2</sup> CH <sub>3</sub> OH: 1.9 mmol/cm <sup>2</sup>	(Qin et al., 2013)
N-doped Ta <sub>2</sub> O <sub>5</sub> (N-Ta <sub>2</sub> O <sub>5</sub> ), linked with electrocatalysts [Ru(dcbpy)(bpy)(CO) <sub>2</sub> ] <sup>2+</sup> or [Ru-(dcbpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	Xe lamp	Ag/AgCl electrode (reference) and glass carbon electrode (counter). Aqueous suspension in MeCN/TEOA at 25 °C.	<b>Quantum yield</b> HCOOH: 1.9%	(Sato et al., 2010)

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